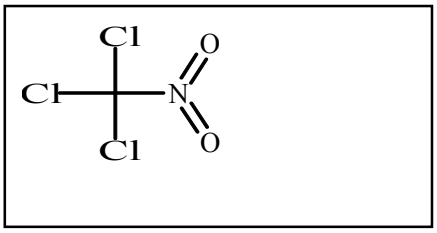
Revised Level I Screening Ecological Risk Assessment for the Reregistration of Chloropicrin

Office of Prevention, Pesticides, and Toxic Substances



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CONVERSION FACTORS

To convert concentrations in air (at 25 °C) from ppm to mg/m^3: mg/m^3 = (ppm) ×(molecular weight of the compound)/(24.45).

I. Executive Summary

A. Nature of Chemical Stressor

Chloropicrin, a pre-plant soil fumigant is used in controlling a broad range of soil pathogens. It is a clear, colorless, nonflammable oily liquid with strong, sharp, highly irritating odor and is a strong lacrimator (tear-producer). Chloropicrin's specific mode of action is not understood, but it is a strong irritant that is very toxic to all biological systems; affecting body surfaces and interfering with the respiratory system and the cellular transport of oxygen (U.S. Forest Service, 1995). Chloropicrin is typically applied once per growing season through soil injection or drip irrigation to fumigate the upper six to twelve inches of soil as a liquid 14 days or more before planting. The maximum application rate is 350 lbs ai/A, with 300 lbs ai/A the maximum for drip irrigation.

B. Conclusions - Exposure Characterization

The high vapor pressure (23.8 mm @ 25°C), high Henry's Law Constant (2.05 X 10^{-3} atm M^3/mole), and low affinity for sorption (K_{oc} 36.05 L kg^{-1}) on soil of chloropicrin suggest that volatilization is the most important environmental route of dissipation. The importance of other competing environmental processes such as leaching, biotic and abiotic degradation, and adsorption to the soil particles will certainly depend on the chloropicrin emission rate, weather conditions, and soil characteristics of the fumigated fields. Fumigant post-application field management practices like splitting, retaining or removing tarp from the fumigated field also determine the amount of chloropicrin that will be available for other competing environmental processes and its residence time in soil. The estimated biodegradation half-lives of chloropicrin in soil range from 4.5 to 10 days, with carbon dioxide being the terminal breakdown product.

Once it volatilized, chloropicrin photolyzes rapidly with an estimated atmospheric half-life of 3.4 to 8 hours in direct sunlight, leading to an estimate of 1 day for its atmospheric lifetime. With an ozone depletion potential more than four orders of magnitude ($5.6x10^{-5}$ versus 0.38) less than the ozone depleting substances such as methyl bromide, chloropicrin is not a threat to stratospheric ozone. The major degradation products were phosgene (carbonyl chloride) and nitrosyl chloride, which rapidly photolyzes to reactive products NO and Cl•. Continued oxidation of the chloropicrin photolysis products would eventually produce CO_2, NO_2, N_2O_4, and Cl_2. The reactive byproducts of chloropicrin photolysis, in particular chlorine free radicals and NO_x, could lead to the generation of tropospheric ozone. Since the metabolites of chloropinrin are very reactive and unstable in the atmosphere, they were not considered in the risk assessment.

Since chloropicrin is highly soluble in water and has low adsorption in soil, residual chloropicrin in soil can potentially leach into groundwater under continuos irrigation and high rainfall events and to surface water through runoff under a flooded condition. The calculated half-life of 31.1 hours is for chloropicrin in aqueous solution (pH 7) when irradiated with a xenon light source, forming carbon dioxide, chloride, nitrate and nitrite. The high Henry's Law

Constant (2.05 X 10^{-3} atm M^3/mole) and rapid photohydrolysis of chloropicrin suggest that volatilization and rapid abiotic degradation are the most important routes of dissipation from surface water. Also, the low octanol/water partition coefficient of chloropicrin indicates that it is not likely to be bioconcentrated in tissues of aquatic organisms. Chloropicrin was found at less than 1.00 µg/L in three wells from 15,175 wells in Florida. However, no monitoring data of chloropicrin in surface water are available at the present time.

C. Potential Risks to Non-target Organisms

This is a Level I screening assessment. EFED has a strong presumption of acute risk to all exposed plants and animals, since chloropicrin is a broad-spectrum fumigant. It is assumed that all living organisms in the treated soil (including beneficial insects and burrowing mammals, for example) are at high risk of mortality. In addition, a wide range of terrestrial and aquatic non-target organisms off-site may also be at risk. Chloropicrin appears to pose risks to mammals and birds based on modeled air residues, exceeding an equivalent acute Level of Concern (LOC) for endangered species. It also exceeds LOCs (including acute endangered species) for fish with all modeled scenarios and for aquatic invertebrates for three of six scenarios. However, there are substantial uncertainties in estimating ecological effects of chloropicrin due to limited toxicity data and the limitations of current exposure models and crop scenarios. The PRZM model also has limited capabilities in capturing the partitions of volatile chemical in air, water and sediment. No fully acceptable toxicity data are available, except for the mammal acute oral and chronic inhalation data used, and thus uncertainty levels are high.

Risks to Aquatic Animals

Of the six modeled scenarios, chloropicrin exceeds Levels-of-Concern (acute endangered species, acute restricted use, and/or acute risk) 1) for fish, with all six scenarios (California tomatoes, California onions, Florida tomatoes, Florida strawberries, North Carolina sweet potatoes, and North Carolina tobacco; risk quotients range from >0.09 to >6.35), and 2) for aquatic invertebrates, with California tomatoes, Florida tomatoes and Florida strawberries (risk quotients range from >0.05 to >1.52 for these crops). Since all toxicity values are considered to be less than the calculated numeric values (because of absent or inadequately measured residues of this volatile chemical), risk quotients are all expressed as greater than the quotient numeric values. EFED thus cannot confirm that any use pattern does not exceed LOCs. Some mortality occurred in the aquatic invertebrate study even at test levels where residues were below the Level of Quantitation at 48 hours. Thus, the above use sites are simply examples of sites that would exceed one or more LOCs even if the actual toxicity values were not lower (i.e., more toxic) than the values used for the risk quotient calculations. These risks would also apply to other aquatic animals such as aquatic phase amphibians. However, in addition to this uncertainty concerning the toxicity of chloropicrin to aquatic animals (i.e., with toxicity values expressed as less than the calculated values, EFED considers chloropicrin to be more toxic than these values), there are also substantial uncertainties concerning exposure modeling values, as described below (in Data Gaps and Uncertainties).

Risks to Terrestrial Animals

The risk to non-target terrestrial animals off-site is primarily from inhalation of chloropicrin off-gassed from treated fields. EFED does not have LOCs specifically for inhalation exposure. However, based on modeled air residues and acute toxicity data available from Health Effects Division, chloropicrin would exceed the existing LOCs for acute risk to endangered species for mammals. Based on the mammal analysis, it is assumed that birds could be at a similar risk. Other terrestrial wildlife (e.g., reptiles and terrestrial phase amphibians) may also be at risk.

Risks to Aquatic and Terrestrial Plants

Although no guideline plant data are available for chloropicrin, label and other information citing phytotoxicity potential on treated sites implies that off-gassed chloropicrin might also pose a risk to terrestrial plants and that modeled aquatic residues might pose a risk to aquatic plants.

D. Conclusions - Effects Characterization

Based on very limited data, chloropicrin is considered very highly toxic to both fish (lowest LC50 < 16.98 ppb) and aquatic invertebrates (lowest LC50 < 71 ppb). The acute mammal inhalation LD50 is 0.114 mg/L (male rats) and the developmental NOAEL in rabbits is 0.003 mg/L (LOAEL 0.008 mg/L, based on abortions and decreased fetal weights). The mammal acute oral LD50 value (used in a preliminary analysis) is 37.5 mg/kg (highly toxic).

E. Data Gaps and Uncertainties

1. Environmental Fate and Exposure

The environmental fate data base for the parent compound provided mostly supplemental information (Appendix F, Table A1-B). However, key environmental fate studies such as aerobic soil metabolism and photolysis in air have several deficiencies and problems. Therefore, data related to these key environmental fate processes were also obtained from open literature to complete the environmental fate and exposure assessment. The following environmental fate study was not submitted, but is not needed for risk assessment.

165-4 Bioaccumulation in fish of chloropicrin The octanol/water partition coefficient (Log K_{ow}) for chloropicrin is 2.38, indicating a low potential for chloropicrin to bioaccumulate in aquatic organisms. It also photolyzed ($t_{1/2}$= 1.3 days) in water rapidly. The bioaccumulation in fish study is not required under these circumstances, according to the Subdivision N guidelines.

Uncertainties

There are uncertainties in estimating chloropicrin exposure in surface water from post-application, due to tarping of the treated area. If tarping is used to minimize the volatilization of chloropicrin, the loading of the chemical through runoff will be limited until the tarp is sliced or removed from the field. The present version of the PRZM model and the selected crop scenarios used in modeling have limited capabilities in discounting the load from runoff of applied chemical under a post-application tarp scenario. PRZM also has limited capabilities in capturing the partitions of a volatile chemical in air, water and sediment. Since the load of chloropicrin from runoff is considered in the PRZM/EXAMS simulation, the estimated concentrations of chloropicrin in surface water bodies may be upper bound.

There are uncertainties with both existing monitoring and modeling of air residues for the purpose of estimating exposure to terrestrial wildlife. Since field emission and air monitoring data of chloropicrin were collected greater than 1 meter above the ground surface, actual concentrations at ground level may differ from estimated air concentration using ISCTS3 modeling and ambient air monitoring . Air monitoring at ground-level of chloropicrin in the fumigated fields may reduce the uncertainty related to terrestrial exposure for wildlife.

2. Ecological Effects

The following data are needed on chloropicrin for ecological risk assessment. These data needs are similar to those available or previously specified as needed for risk assessment for methyl bromide and for the degradate MITC as part of the metam-sodium risk assessment. Appendix E lists the status of the ecological effects data requirements for chloropicrin.

71-1 Avian Acute Oral. The current estimate of avian risk is based largely on the mammal assessment. This basic study will contribute to a risk assessment specific to birds. It will 1) enable a comparison to the mammal acute oral data and 2) enable the use of an EFED spreadsheet to estimate avian acute inhalation toxicity based on the mammal acute oral and inhalation data.

----- Avian acute inhalation. The current estimate of avian risk is based largely on the mammal assessment. This study will enable an inhalation risk assessment specific to birds. Since the risk assessment for terrestrial wildlife is focused on inhalation and this study will provide actual inhalation data rather than an estimation based on acute oral data, it is of even higher priority than the acute oral study.

-----Avian sub-chronic/chronic inhalation. This study is needed for risk assessment, due to the potential for repeat and/or continuous exposure to birds resulting from the use of chloropicrin on multiple fields over multiple days in any given geographic area.

870.1300. Acute inhalation toxicity test – rat.. The existing study (MRID 45117902) is classified by HED as Acceptable/Non-guideline. The 7/25/00 DER and 1/31/05 Revised HED Human Health Risk Assessment state: "The LC50 calculated for the study should not be considered to be a true LC50 for chloropicrin. Due to the sacrifice of all live animals at day 3 of the study instead of day 14, and too large of exposure particle sizes, the true LC50 could be lower." Thus, a new study will enable an improved wild mammal risk assessment with reduced uncertainty. Please note that although EFED needs the results this study for risk assessment, it is not listed in Appendix E since it is an HED guideline and EFED does not review these studies.

72-1(a) and (c) Acute Fish Toxicity – bluegill and rainbow trout. The risk assessment is currently relying on supplemental data, with indeterminate toxicity values. Flow-through studies with measured concentrations will greatly reduce uncertainty.

72-2(a) Acute aquatic invertebrate toxicity. The risk assessment is currently relying on supplemental data, with indeterminate toxicity values. Flow-through studies with measured concentrations will greatly reduce uncertainty.

72-3(a) Acute Marine/Estuarine Fish. Given the use patterns of chloropicrin, marine/estuarine species could be exposed. This study will enable a risk assessment specific for marine/estuarine species exposure.

72-3(b) Acute Marine/Estuarine Mollusk. Given the use patterns of chloropicrin, marine/estuarine species could be exposed. This study will enable a risk assessment specific for marine/estuarine species exposure. It will also improve certainty with the endangered species risk assessment, as this test species may be more representative of endangered freshwater mussels than the freshwater *Daphnia*.

72-3 (c) Acute Marine/Estuarine Shrimp. Given the use patterns of chloropicrin, marine/estuarine species could be exposed. This study will enable a risk assessment specific for marine/estuarine species exposure. One literature search toxicity value is available, but it is from a static study without measured concentrations.

72-4(a) Early Life-stage Fish – Freshwater. Current aquatic modeling indicates the potential for chronic aquatic exposure to chloropicrin. This study will enable a chronic risk assessment for freshwater fish.

72-4(a) Early Life-stage Fish – Marine/Estuarine. Current aquatic modeling indicates the potential for chronic aquatic exposure to chloropicrin. This study is reserved pending the submission and review of the above early life-stage studies with a freshwater fish species.

72-4(b) Life-Cycle Aquatic Invertebrate. Current aquatic modeling indicates the potential for chronic aquatic exposure to chloropicrin. This study will enable a chronic risk assessment for

aquatic invertebrates.

72-5 Life-Cycle Fish. This study is reserved, pending submission and review of early life-stage fish testing.

123-1(a) Seed Germination/Seedling Emergence – Tier II. Chloropicrin is used in part due to its phytotoxicity at the application site, and a wide range of open literature and other non-guideline studies indicate the potential for plant damage. This study will enable the assessment of risk to non-target terrestrial plants off-site.

123-1(b) Vegetative Vigor – Tier II. Chloropicrin has at least some phytotoxicity on the treatment site, based on label and open literature information. This study will enable the assessment of risk to non-target terrestrial plants off-site.

123-2 Aquatic Plant Growth – Tier II. Chloropicrin has at least some phytotoxicity on the treatment site, based on label and open literature information. This study will enable the assessment of risk to non-target aquatic plants off-site.

141-1 Honeybee Acute contact. This basic study is now being requested for virtually all outdoor uses, and will help determine the need for, and specifics of, bee hazard labeling.

Uncertainties

There are substantial uncertainties concerning the ecological effects of chloropicrin, in part due to the extremely limited data available for risk assessment. There are no studies considered fully acceptable for any taxonomic group or time exposure, except for the mammal acute oral and chronic inhalation data used.

The uncertainties associated with the risk to terrestrial organisms from chloropicrin use are mainly focused on the extent and effect of terrestrial animal exposure via inhalation. There is uncertainty with the mammal acute inhalation toxicity, as indicated above. Avian inhalation toxicity data are not available at all, as also noted. In addition, the lack of avian acute oral data prevents an extrapolated estimation of inhalation toxicity based on mammal data. Terrestrial plant data are needed to conduct an assessment of risk to non-target terrestrial plants off-site.

Because of the repeat exposures from applications to different fields on different days in a given geographic area, there is the added potential for chronic exposure. Acute inhalation studies are typically just 4 hours long. A subchronic/chronic avian inhalation study will enable EFED to address longer-term exposure to birds.

The uncertainties associated with the risk to aquatic organisms from chloropicrin are due to uncertainties over the length of exposure to this highly volatile chemical and to uncertainties over the toxicity (resulting mainly from the volatility). However, both acute and chronic

exposure are possible, in part due to repeat or continuous input to the aquatic environment. Acute and chronic toxicity data are not available for most fish and aquatic invertebrate guideline test categories, freshwater or estuarine/marine. The risk assessment relies on supplemental data for freshwater fish and aquatic invertebrates.

II. Problem Formulation

A. Stressor Source and Distribution

1. Source and Intensity

The source of the stressor considered in this ecological risk assessment is the sole active ingredient chloropicrin, a pre-plant fumigant used in controlling soil pathogens. Chloropicrin is a small, single-carbon organic molecule that diffuses rapidly and volatilizes from applied agricultural soils. The major source and mechanism of release of chloropicrin is volatilization from the fumigated sites. Additional transport mechanisms include runoff from pre-plant fumigated fields, and drift of volatilized chloropicrin and redeposition through precipitation in the adjacent area. The major breakdown products of chloropicrin in soil and air is carbon dioxide. Since the degradation products of chloropicrin are unstable in the environment, no metabolites were considered in the risk assessment.

2. Physical/Chemical/Fate and Transport Properties

Chloropicrin is a clear, colorless, nonflammable oily liquid with strong, sharp, highly irritating odor and a strong lacrimator. The high vapor pressure (23.8 mm @ 25°C), high Henry's Law Constant ($2.05 * 10^{-3}$ atm M^3/mole), and low affinity for sorption on soil of chloropicrin suggest that volatilization is the most important environmental route of dissipation. Chloropicrin also undergoes rapid breakdown in soil, primarily via microbial degradation as well as in the atmosphere through direct photolysis. The relatively low K_{ow} and high water solubility of the parent suggests bio-concentration in aquatic organisms will be low.

3. Pesticide Type, Class, and Mode of Action

Chloropicrin is a fumigant used in pre-plant soil fumigation. Chloropicrin's specific mode of action is not understood, but it is a strong irritant that is very toxic to all biological systems; affecting body surfaces and interfering with the respiratory system and the cellular transport of oxygen (U.S. Forest Service, 1995).

4. Overview of Pesticide Usage

Pre-plant soil use in agriculture accounts for most of the use of chloropicrin. Chloropicrin can also be formulated in combination with other fumigant to broaden its spectrum. In these combination end-use products, the percent active ingredient for chloropicrin can range from 20 to 55% when combined with methyl bromide and from 15 to 60% when combined with 1,3-D. Chloropicrin is typically applied once per growing season through soil injection or drip irrigation to fumigate upper six to twelve inches of soil as a liquid 14 days or more before planting. The maximum application rate is 350 lb ai/A, with 300 lb ai/A the maximum for drip irrigation. The

product is also used as a warning agent for odorless fumigants. Individually, strawberries, tobacco, tomatoes, and peppers were the crops with the highest percentage of their overall acreage treated from 1998 to 2000.

B. Receptors

1. Ecological Effects

Each assessment endpoint requires one or more measures of ecological effect, which are defined as changes in the attributes of an assessment endpoint itself or changes in a surrogate entity or attribute in response to exposure to a pesticide. Ecological measures of effect for the screening level risk assessment are usually based on a suite of registrant-submitted toxicity studies performed on a limited number of organisms in broad groupings listed in **Table 1**. These laboratory test organisms serve as surrogates for all nontarget animal and plant species that could potentially be exposed to a given pesticide.

Table 1. Examples of taxonomic groups and test species evaluated for ecological effects in screening level risk assessments.

Taxonomic Group	*Example(s) of Representative Species*
Birds[1]	*mallard duck (Anas playtrhynchos)* *bobwhite quail (Colinus virginianus)*
Mammals	*laboratory rat*
Freshwater Fish[2]	*bluegill sunfish (Lepomis macrochirus)* *rainbow trout (Oncorhynchus mykiss)*
Freshwater Invertebrates	*water flea (Daphnia magna)*
Estuarine/Marine Fish	*sheepshead minnow (Cypridodon variegatus)*
Estuarine/Marine Invertebrates	*Eastern Oyster (Crassostrea virginica)* *Mysid Shrimp (Americamysis bahia)*
Terrestrial Plants[3]	*Monocots - corn (Zea mays)* *Dicots - soybean (Glycine max)*
Aquatic Plants and Algae	*duckweed (Lemna gibba)* *green algae (Selenastrum capricornutum)*

[1] Birds may be surrogates for amphibians (terrestrial phase) and reptiles.
[2] Freshwater fish may be surrogates for amphibians (aquatic phase).
[3] Four species of two families of monocots, of which one is corn; six species of at least four dicot families, of which one is soybeans.

Within each of these very broad taxonomic groups, an acute and/or chronic endpoint is selected from the available test data. A complete discussion of all toxicity data available for this risk assessment and the resulting measures of effect selected for each taxonomic group are

included in Appendix C. A summary of the potential assessment endpoints and measures of effect selected to characterize potential ecological risks associated with exposure to chloropicrin is provided in **Table 2**. However, data are not available for all potential measures of effect.

Table 2. Summary of potential assessment endpoints and measures of effect.

Assessment Endpoint	Measures of Effect
1. Abundance (i.e., survival, reproduction, and growth) of individuals and populations of birds	1a. Bobwhite quail or mallard duck acute oral LD_{50}
	1b. Bobwhite quail and mallard duck subacute dietary LC_{50}
	1c. Bobwhite quail or mallard duck acute inhalation LC_{50}
	1d. Bobwhite quail and mallard duck chronic reproduction NOAEL and LOAEL
	1e. Bobwhite quail or mallard duck sub-chronic/chronic inhalation toxicity
2. Abundance (i.e., survival, reproduction, and growth) of individuals and populations of mammals	2a. Laboratory rat acute oral LD_{50}
	2b. Laboratory rat acute inhalation toxicity
	2c. Laboratory rat developmental and chronic (2-generation) NOAEL and LOAEL
	2d. Laboratory mammal chronic inhalation NOAEL and LOAEL
3. Survival and reproduction of individuals and communities of freshwater fish and invertebrates	3a. Rainbow trout and bluegill sunfish acute LC_{50}
	3b. Rainbow trout chronic (early-life) NOAEL and LOAEL
	3c. Water flea (and other freshwater invertebrates) acute EC_{50}
	3d. Water flea chronic (life-cycle) NOAEL and LOAEL
4. Survival and reproduction of individuals and communities of estuarine/marine fish and invertebrates	4a. Sheepshead minnow acute LC_{50}
	4b. Estimated chronic NOAEL and LOAEL values based on the acute-to-chronic ratio for freshwater fish
	4c. Eastern oyster and mysid shrimp acute LC_{50}
	4d. Mysid shrimp chronic (life-cycle) NOAEL and LOAEL
	4e. Estimated NOAEL and LOAEL values for mollusks based on the acute-to-chronic ratio for mysids

Table 2. Summary of potential assessment endpoints and measures of effect.

Assessment Endpoint	Measures of Effect
5. Perpetuation of individuals and populations of non-target terrestrial and semi-aquatic species (crops and non-crop plant species)	5a. Monocot and dicot seedling emergence and vegetative vigor EC_{25} values
6. Survival of beneficial insect populations	6a. Honeybee acute contact LD_{50}
7. Maintenance and growth of individuals and populations of aquatic plants from standing crop or biomass	7a. Algal and vascular plant (i.e., duckweed) EC_{50} values for growth rate and biomass measurements

LD_{50} = Lethal dose to 50% of the test population.
NOAEL = No observed adverse effect level.
LOAEL = Lowest observed adverse effect level.
LC_{50} = Lethal concentration to 50% of the test population.
EC_{50}/EC_{25} = Effect concentration to 50%/25% of the test population.

2. Ecosystems Potentially At Risk

Ecosystems potentially at risk are expressed in terms of the selected assessment endpoints. The typical assessment endpoints for screening-level pesticide ecological risks are reduced survival, and reproductive and growth impairment for both aquatic and terrestrial animal species. Aquatic animal species of potential concern include freshwater fish and invertebrates, estuarine/marine fish and invertebrates, and amphibians. Terrestrial animal species of potential concern include birds, mammals, beneficial insects, and earthworms. For both aquatic and terrestrial animal species, direct acute and direct chronic exposures are considered. In order to protect threatened and endangered species, all assessment endpoints are measured at the individual level, which may also provide insights regarding risks at higher levels of biological organization (e.g., populations and communities). For example, pesticide effects on individual survivorship can have important implications for both population growth rates and habitat carrying capacity.

For terrestrial plants and plants in semi-aquatic environments, the screening assessment endpoint is the perpetuation of populations of non-target species, including crops and non-crop plant species. Existing testing requirements focus on an evaluation of seedling emergence and vegetative vigor. The Agency recognizes that these endpoints may not address all components of the lifecycle of plants in terrestrial and semi-aquatic environments. It is assumed that impacts at emergence and in active growth stages can reduce a plant's overall ability to be competitive, ultimately impacting reproductive success.

For aquatic plants, the assessment endpoint is the maintenance and growth of standing

crop or biomass. Measures of effect for these assessment endpoints include growth rates and biomass measurements of algae and common vascular plants (i.e., duckweed). These receptors are useful indicators of risks to the ecosystem for at least two reasons: 1) complete exposure pathways exist for these receptors; and 2) they are ubiquitous, potentially inhabiting areas where pesticides are applied, or areas where runoff and/or spray drift may occur.

Specifically for chloropicrin, ecosystems potentially at risk would include those in close enough proximity to treated fields to receive either off-gassed chloropicrin transported via the air or chloropicrin transported via ground or surface water. Given the use of chloropicrin in multiple states and regions across the U.S. (See Figure 2), this could potentially include a wide variety of terrestrial and aquatic ecosystems

C. Assessment Endpoints

Assessment endpoints are defined as "explicit expressions of the actual environmental value that is to be protected." Defining an assessment endpoint involves two steps: 1) identifying the valued attributes of the environment that are considered to be at risk; and 2) operationally defining the assessment endpoint in terms of an ecological entity (i.e., a community of fish and aquatic invertebrates) and its attributes (i.e., survival and reproduction). Therefore, selection of the assessment endpoints is based on valued entities (i.e., ecological receptors), the ecosystems potentially at risk, the migration pathways of pesticides, and the routes by which ecological receptors are exposed to pesticide-related contamination. The selection of clearly defined assessment endpoints is important because they provide direction and boundaries in the risk assessment for addressing risk management issues of concern. Potential assessment endpoints and measures of effect are described in **Table 2**.

D. Conceptual Model

1. Risk Hypotheses

Risk hypotheses are specific assumptions about potential adverse effects (i.e., changes in assessment endpoints) and may be based on theory and logic, empirical data, mathematical models, or probability models (USEPA 1998a). For this assessment, the risk is stressor-initiated, where the stressor is the release of chloropicrin to the environment. The following risk hypothesis is presumed for this screening level assessment:

> *Based on the toxicity, the high application rates, the volatility, and the environmental fate and mode of action of chloropicrin, as well as the exposed aquatic and terrestrial ecosystems, chloropicrin has the potential to cause reduced survival, and reproductive and growth impairment for both aquatic and terrestrial animal and plant species.*

Adequate protection is defined as protection of growth, reproduction, and survival of

aquatic and terrestrial animal and plant populations, and individuals of threatened and endangered species, as needed.

2. Diagram

The conceptual site model is a generic graphic depiction of the risk hypothesis, and assumes that as a fumigant with a toxic mode of action, chloropicrin is capable of affecting terrestrial and aquatic organisms provided that environmental concentrations are sufficiently elevated as a result of proposed label uses. However, through a preliminary iterative process of examining fate and effects data, the conceptual model, i.e., the risk hypothesis, has been refined to reflect the likely exposure pathways and the organisms that are most relevant and applicable to this assessment (**Figure 1**). It includes the potential pesticide or stressor (chloropicrin), the source and/or transport pathways, abiotic exposure media, exposure point, biological receptor types, and attribute changes.

In order for a chemical to pose an ecological risk, it must reach ecological receptors in biologically significant concentrations. An exposure pathway is the means by which a contaminant moves in the environment from a source to an ecological receptor. For an ecological exposure pathway to be complete, it must have a source, a release mechanism, an environmental transport medium, a point of exposure for ecological receptors, and a feasible route of exposure. In addition, the potential mechanisms of transformation (i.e., which degradates may form in the environment, in which media, and how much) must be known, especially for a chemical whose metabolites/degradates are of greater toxicological concern than the parent compound. The assessment of ecological exposure pathways, therefore, includes an examination of the sources and potential migration pathways for constituents, and the determination of potential exposure routes (e.g., ingestion, inhalation, dermal absorption).

The source and mechanism of release of chloropicrin are volatilization, drift and runoff from pre-plant fumigated fields for agricultural crops. Surface water runoff from the areas of application is assumed to follow topography. Additional transport mechanisms include drift of volatilized chloropicrin as well as redeposition through precipitation to the surrounding areas. Chloropicrin exposure to terrestrial animals is expected primarily through inhalation of chloropicrin and to a lesser extent by ingestion of contaminated food items such as grass and foliage contaminated from atmospheric redeposition. Exposure from

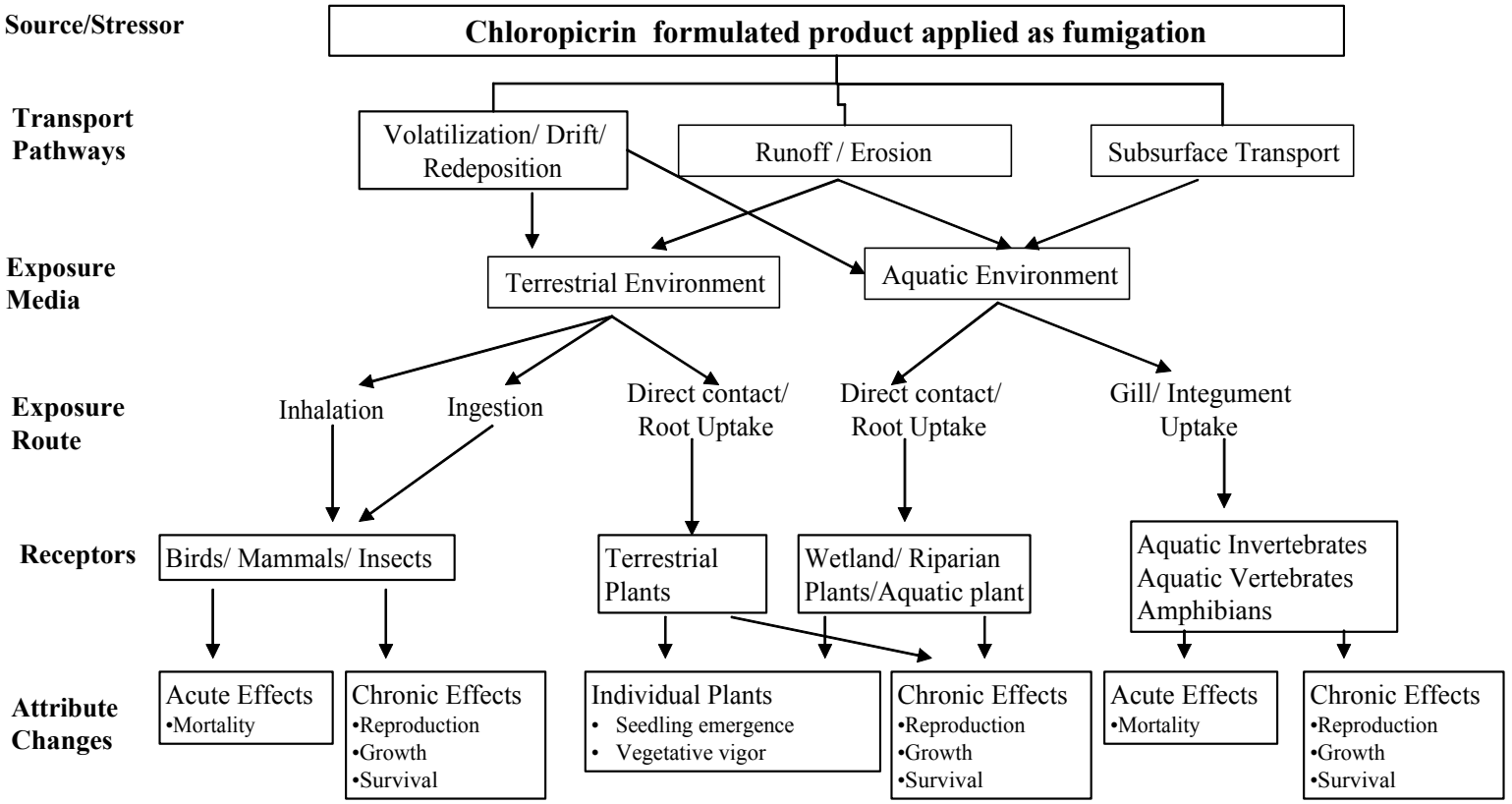


Figure 1. Conceptual model depicting potential sources and routes of uptake for chloropicrin (stressor), potential interaction with nontarget animals and plants (receptors), and potential changes in the biological receptor attributes

redeposition of volatilized chloropicrin via precipitation in terrestrial environment is expected to be negligible, due to the short direct photolytic half-life (($t_{1/2}$ <8 hrs) of chloropicrin in the atmosphere. Thus, the exposure from redeposition of chloropicrin via precipitation was not considered in this assessment.

Ecological receptors that may potentially be exposed to chloropicrin include terrestrial and semi-aquatic wildlife (i.e., mammals, birds, and reptiles), terrestrial plants and plants in semi-aquatic areas, and soil invertebrates. In addition to terrestrial ecological receptors, aquatic receptors (e.g., freshwater and estuarine/marine fish and invertebrates, amphibians) may also be exposed to potential migration of pesticide from the site of application to various watersheds and other aquatic environments via runoff and drift of volatilized material. For aquatic receptors, the major point of exposure is through direct contact with the water column, sediment, and pore water (gill/integument) contaminated with spray drift and/or runoff from treated areas. However, indirect effects to aquatic organisms (especially fish) can also occur through impact to various food chains.

There are substantial uncertainties concerning the ecological effects of chloropicrin, in part due to the extremely limited ecotoxicity data available. There are no studies considered fully acceptable for any taxonomic group or time exposure, except the mammal acute oral and chronic inhalation data used. Therefore, the evaluation of risk to various taxonomic groups is based on very limited toxicity data.

E. Analysis Plan

1. Preliminary Identification of Data Gaps and Methods

The analysis plan is the final step in Problem Formulation and targets the working hypotheses that are considered more likely to effect the assessment endpoints. The Analysis Plan specifies the data that is required in developing an evaluation of the potential impact of a pesticide to the assessment endpoints and the methods that will be used to analyze the data. The Analysis Plan is also used to outline the scope of the assessment, identify the measures of effect to be used in evaluating the hypothesis, and a rationale for the focus and possible refinement of the assessment.

The objective of EFED's risk assessment is to identify the risk to the environment from chloropicrin use as a soil fumigant in agricultural crops. This initial analysis will be referred to as Tier I screening and is based on the ratio or quotient method. As noted in the USEPA 1998, Part A Section 5.1.3, "Typically, the ratio (or quotient) is expressed as an exposure concentration divided by an effects concentration". Therefore the risk quotient (RQ) is the ratio of the estimated environmental concentration (EEC) of a chemical to a toxicity test effect (e.g., LC_{50}) for a given species. The RQ as an index of potential adverse effects is then compared to an Agency established Level of Concern (LOC) in order to identify when the potential adverse

effect is a concern to the Agency. These LOCs are the Agency's interpretive policy and are used to analyze potential risk to non-target organisms and the need to consider regulatory action. Appendix D of this document summarizes the LOCs used in this risk assessment. This paper presents a sequence of risk assessment methods that include PRZM/EXAMS generated EEC values for aquatic exposure and ISCTS3 model simulated air residue values for terrestrial wildlife exposure. The laboratory-derived effects data for the most sensitive representative species of terrestrial and aquatic organisms are included in Tables 9 and 10**.** This screening-level assessment should identify habitats, and species potentially at risk from chloropicrin exposure. The fate, effects, and usage information presented in this document suggest that the focus of the working hypothesis for an environmental risk assessment is that exposure to chloropicrin has the potential to cause acute and chronic effects that may result in reduced survival, reproductive impairment and growth effects to aquatic and terrestrial animals and plant species.

Data Gaps

The adequacy of the submitted data was evaluated relative to Agency guidelines. The following identified data gaps for ecological fate and effects endpoints result in a degree of uncertainty in evaluating the ecological risk of chloropicrin.

- No data are available to assess the acute or chronic risk of chloropicrin to birds.
- No data are available to assess the chronic risk of chloropicrin to freshwater or estuarine/marine fish.
- No data are available to assess the chronic risk of chloropicrin to freshwater or estuarine/marine invertebrates.
- No data are available to assess the risk of chloropicrin to terrestrial, aquatic, or semi-aquatic plants.
- The mammal acute inhalation study reviewed by HED has deficiencies and is considered non-guideline.
- Studies available on the effects of chloropicrin to freshwater fish and aquatic invertebrates are considered supplemental, with indeterminate toxicity values (i.e., "<").

2. Measures to Evaluate Risk Hypotheses and Conceptual Model

a. Measures of Exposure

Exposure concentrations for aquatic ecosystems were estimated based on the Tier 2 aquatic model Pesticide Root Zone Model(PRZM; Carsel, et al., 1998) and Exposure Analysis

Modeling System (EXAMS; Burns, 2002). PRZM (version 3.12 Beta compiled May 24, 2001) 2001) simulates the fate of the chemical in the field, including runoff and erosion on a daily time step, and EXAMS (version 2.98.04 compiled November 2002) simulates the environmental fate and transport processes in a body of surface water. A graphical user interface (pe4v01.pl), developed by the USEPA, 2004 was used to facilitate the input of chemical, fate, and use specific parameters into the appropriate PRZM and EXAMS files. PRZM/EXAMS model simulates are run for multiple (usually 30) years and reported estimated environmental concentration (EEC) are the concentrations that are expected once in every ten years based on the thirty years of daily values generated by the simulation. The critical measure of exposure for a Tier 1 acute aquatic risk assessment is the peak EEC in surface water. For chronic aquatic assessments, the 21-day average EEC is typically used for aquatic invertebrates and the 60-day average is now typically used for fish (both embryo-larvae and full lifecycle).

Exposure concentrations for terrestrial ecosystems were based on estimated atmospheric concentrations of chloropicrin using the Industrial Source Complex - Short Term (ISCST3) air dispersion model developed by USEPA (USEPA, 1995). The modeling approaches used by the Agency were based on 24 hours exposure intervals (i.e., 24 hours time-weighted average of monitored air concentration of chloropicrin at the edge of the fumigated field. Field sizes includes 1-, 5-, 10-, 20-, and 40 acre squares to represent a cross section of the fields that might be fumigated for agriculture use. ISCST3 model was used in estimating air concentration using field emission ratio (ratio of the flux rate to the application rate), various sized fields, methods of chloropicrin placement, and different meteorological conditions. The estimated maximum concentration of 0.019 mg/L (19037 $\mu g/m^3$) was used in calculating inhalation exposure for terrestrial organisms.

b. Measures of Effect

Measures of effect are generally based on the results of a toxicity study, although monitoring data and incident reports may also be used to provide supporting lines of evidence for the risk characterization. A complete summary of the potential measures of effect based on toxicity studies for different ecological receptors and effect endpoints (acute/chronic) is given in **Table 2** above. Examples of measures of acute effects (e.g., lethality) include an oral LD_{50} for mammals and LC_{50} for fish and invertebrates. Examples of measures of chronic effects include a NOAEL for birds or mammals based on reproduction or developmental endpoints, and an EC_{05} for plants based on growth rate or biomass measurements.

c. Measures of Ecosystem and Receptor Characteristics

For the Tier 1 assessment, the ecosystems that are modeled are intended to be generally representative of any aquatic or terrestrial ecosystem associated with areas where chloropicrin is used. The receptors addressed by the aquatic and terrestrial risk assessments are summarized in **Figure 1**. For aquatic assessments, generally fish, aquatic invertebrates, and aquatic plants in

both freshwater and estuarine/marine environments are represented. For terrestrial assessments, generally birds, terrestrial plants, and wild mammals are included.

III. Analysis

A. Use Characterization

Chloropicrin is a broad-spectrum fumigant used for the control of weeds, nematodes, insects, rodents, and certain fungi. Chloropicrin end-use products are packaged as 100% chloropicrin formulations as well as in combination formulations with methyl bromide and 1,3-D. In these combination end-use products, the percent active ingredient for chloropicrin can range from 20 to 55% when combined with methyl bromide and from 15 to 60% when combined with 1,3-D.

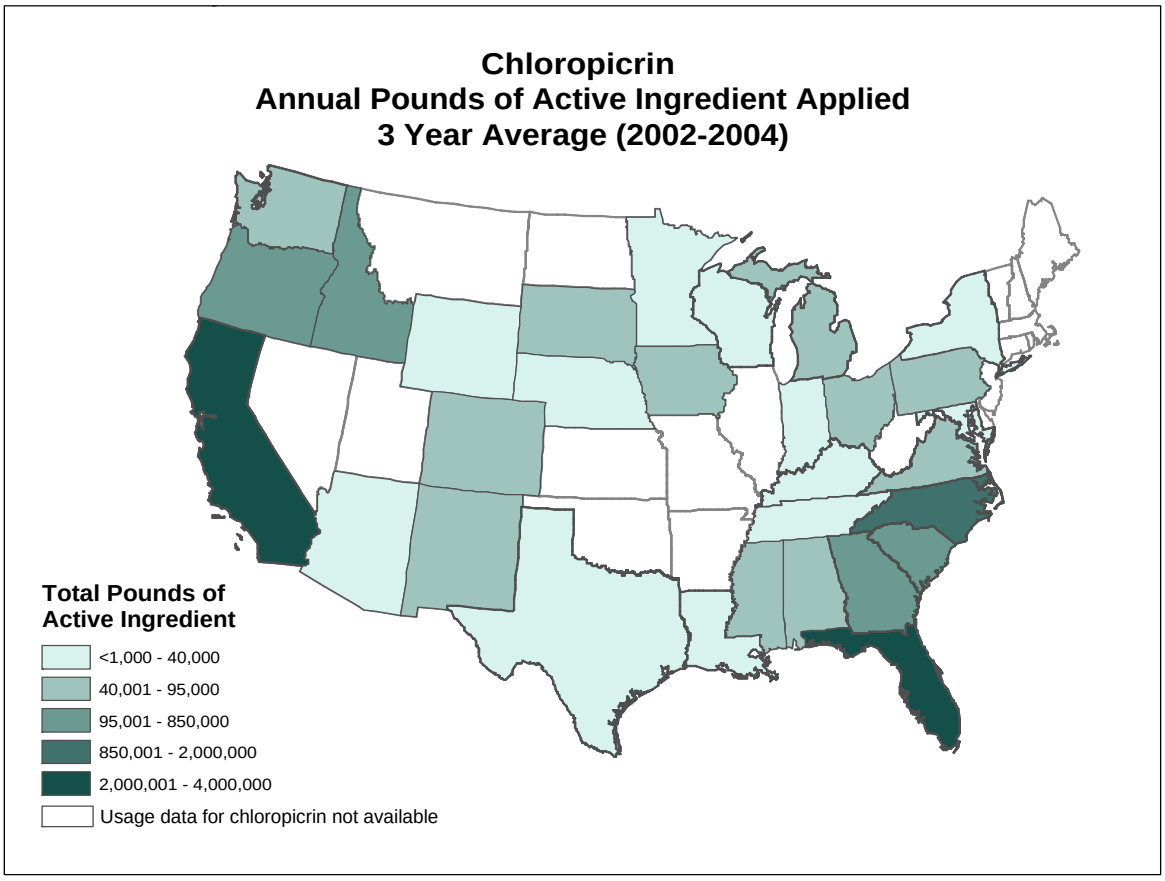
Chloropicrin is registered for pre-plant soil fumigation of field to be planted with a wide variety of food, ornamental, and nursery crops. Typical use consists of making one application per year prior to planting a crop or multiple crops in the fumigated field. Individually, strawberries, tobacco, tomatoes, and peppers were the crops with the highest percentage of their overall acreage treated from 1998 to 2000. The average annual percent crop treated for those crops, respectively, were 20, 15, 10, and 10 percent while the maximum percent crop treated, respectively, for those crops was 50, 20, 45, and 30 percent. Crops that use over a million pounds annually of chloropicrin in their production include tobacco (3.6 million pounds), tomatoes (1.7 million pounds), and strawberries (1.4 million pounds). Figure 2 shows the average pounds of active ingredient was applied in various states for all surveys crops based on three years (2002 to 2004) of EPA data (USEPA 2005a).

In general, two most frequent options of chloropicrin application methods include shank injection (soil injection) followed by tarping and drip irrigation (chemigation) under a pre-tarped soil surface. Chloropicrin can also be applied using shank injection and drip irrigation without tarping. Non-tarp shank injection application requires lower rate (≤175 lbs/acre) of chloropicrin, possibly due to requirements for worker protection. For drip irrigation, non-tarp chloropicrin application in soil requires the placement of drip tubing at a minimum depth of 5 inches from surface. Post application sealing methods like tarping, water sealing, and compacting soil surface are fumigant management practices followed immediately after fumigation to contain the applied chloropicrin and reduce its diffusion into the atmosphere.

The Chloropicrin Manufacturer's Task Force (CMTF) members have amended the four existing manufacturing labels to use in delete use of chloropicrin as an active ingredient in pesticide formulations for post-harvest uses, structural fumigations, forestry uses, and aquatic use patterns. The CMTF is supporting pre-plant soil fumigation use in agricultural fields and commercial greenhouses. In addition to this labeling change, CMTF is supporting the following maximum rates for pre-plant soil fumigation use in agricultural field.

- 350 lbs per treated acre for shank injection applications - tarped;
- 175 lbs per treated acre for shank injection applications - untarped;
- 300 lbs per treated acre for drip irrigation applications.

Figure 2. Average annual pounds of active ingredient of chloropicrin was applied by state for all surveyed crops based on three years of EPA data (2002-2004).



There are some current chloropicrin labels that have higher maximum application rates but CMTF has not conducted studies to support these higher rates. At this time, the assessment reflects these new maximum rates. Other registrants wishing to support higher rates must conduct the appropriate studies and submit them to the Agency.

Chloropicrin is also used as an odorant when it is added to methyl bromide (for pre-plant soil fumigation) and sulfuryl fluoride (indoor fumigation) formulations at 2% by weight or less. When used in this capacity, chloropicrin is not used as an active ingredient but as a warning agent to indicate possible hazardous concentrations of odorless methyl bromide or sulfuryl fluoride vapors.

B. Exposure Characterization

1. Environmental Fate and Transport Characterization

Chloropicrin is a clear, colorless, nonflammable oily liquid with strong, sharp, highly irritating odor and a strong lacrimator. Selected physic-chemical and environmental fate properties of chloropicrin are listed in Table 3 and 4. The high vapor pressure (23.8 mm @ 25°C), high Henry's Law Constant (2.05 X 10^{-3} atm M^3/mole), and low soil adsorption coefficient (K_{oc} 36.05 L kg^{-1}) on soil of chloropicrin suggest that volatilization is the most important environmental route of dissipation. Direct photolytic degradation ($t_{1/2}$ <8 hrs) of chloropicrin is the primary route of dissipation in the atmosphere, which suggest it is not a significant threat to deplete stratosphere ozone layer. Due to the fact that volatilization is significant and occurs rapidly, the importance of other competing processes such as leaching, biotic and abiotic degradation, and adsorption to the soil particles will certainly depend on chloropicrin emission rate from fumigated fields. This is because emission rate determines the amount of chloropicrin left for other processes and its residence time in the soil system. However, if chloropicrin remains in soil, it also degrades in soil with half-lives ranges from 4.5 to 10 days with CO_2 being the terminal breakdown product. Since chloropicrin is highly soluble in water and has low adsorption in soil, it can potentially leach into groundwater and to surface water through runoff under a flooded condition. The low octanol/water partition coefficient of chloropicrin also indicates that it is not likely to be bioconcentrated in tissues of aquatic organisms.

Table 3: Selected physical and chemical properties of chloropicrin

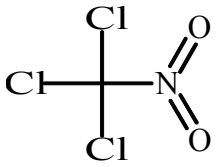
Parameter	Value	Reference
Chemical Structure		
PC Code	081501	
CAS number	76-06-2	
Common name	Chloropicrin	
SMILES Notation	N(=O)(=O)C(CL)(CL)CL	
Molecular formula	CCl_3NO_2	MRID# 43613901
Molecular weight	164.38 g/mol	MRID# 43613901
IUPAC name	trichloronitromethane	Merck Index
CAS name	trichloronitromethane	Merck Index

Table 3: Selected physical and chemical properties of chloropicrin

Parameter	Value	Reference
Physical State	Near colorless, oily liquid	Merck Index
Melting point/range	-69.2□C	Merck Index
Boiling point/range	112□C at 757 mm Hg	Merck Index
Density	1.7 g/mL at 25 □C	Merck Index
Water solubility	1.612 g/L @ 25°C	MRID# 43613901
Vapor pressure	23.8 mm Hg at 25 □C	Merck Index
Henry's Law Constant@ 25°C	2.05 * 10^{-3} atm•m^3/mole	Kawamoto and Urano, 1989
Octanol/water partition coefficient (Log K_{OW})	2.38	Kawamoto and Urano, 1989

Table 4. Environmental Fate Properties of Chloropicrin

Parameter	Value	Reference/Comments
Hydrolysis $t_{1/2}$	Stable at pH 5, 7, and 9	MRID# 43022401
Photolysis $t_{1/2}$ in water	1.3 days, degradates chloride, nitrate, nitrite, and CO_2	MRID# 42900201
Photolysis $t_{1/2}$ on soil	N/A	Waived
Photolysis $t_{1/2}$ in air	≤8.0 Hours	Carter et al., 1997
	20 days phosgene ($COCl_2$), nitrosyl chloride (NOCl), nitrous oxide (NO), and chlorine (Cl_2); subsequently nitrogen dioxide (NO_2) and dinitrogen tetraoxide (N_2O_4)	MRID# 05007865
Soil metabolism Aerobic $t_{1/2}$	4.5 days	Wilhelm et al., 1996
	10 days major degradate is CO_2 minor degradates (total <6%) chloronitromethane, nitromethane, and bicarbonate	MRID# 43613901
Aquatic metabolism Anaerobic $t_{1/2}$	1.3 hours major degradates nitromethane and chloronitromethane	MRID# 43759301

Table 4. Environmental Fate Properties of Chloropicrin

Parameter	Value	Reference/Comments
Aquatic metabolism Aerobic $t_{1/2}$	N/A	Waived
K_{OC}	36.05 L kg^{-1}	EPISUITE
Laboratory Volatility	Non-tarped soil maximum volatility 342 µg/cm^2/hr; Tarped soil maximum volatility 205 µg/cm^2/hr	MRID# 43798601
Terrestrial Field Dissipation	≤1.4 days from 3- to 12-inch depth from a sandy loam and a sand from California, measured after tarp was removed	MRID# 43085101
Aquatic Field Dissipation	N/A	Waived
Accumulation in Fish, max. BCF	N/A	Waived

(a) Fate and Transport in soil and water

The dissipation of chloropicrin in aquatic and terrestrial environments appears to be predominantly dependent on volatilization and to a lesser extent on leaching and degradation. The high vapor pressure and the high Henry's Law Constant suggests that chloropicrin will volatilize from soil and water. Once it volatilized, chloropicrin degrades rapidly into CO_2 and other metabolites in the atmosphere via direct photolysis. The importance of other competing processes such as leaching, biodegradation, and adsorption to the soil particles will certainly depend on chloropicrin emission rate from the fumigated fields. This is because emission rate determines the amount of chloropicrin left for other processes and its residence time in the soil system. The biodegradation half-lives of chloropicrin is 10 days with carbon dioxide being the terminal breakdown product (MRID 43613901). Also, a cursory review of literature data (Wilhelm et al., 1996, Gan et al., 2000) shows that major metabolic pathways occurs through successive reductive dehalogenation of chloropicrin to nitromethane:

$$\mathbf{CCl_3NO_2 \rightarrow HCCl_2NO_2 \rightarrow H_2CClNO_2 \rightarrow H_3CNO_2 \rightarrow CO_2}$$

Degradation of chloropicrin in soil follows first-order kinetics. Wilhelm et al.(1996)

estimated the half-life of 4.5 days for chloropicrin in sandy loam soil with a rate equivalent to 500 lbs/Acre following the Agency's Pesticide Assessment Guidelines. Gan et al. (2000) estimated that microbial degradation accounted for 68 to 92 percent of the overall degradation of applied chloropicrin.

Chloropicrin is highly soluble in water and are weakly retained by soil. The supplemental terrestrial field dissipation studies (MRID 43085101) were conducted in California, applying chloropicrin to bare fallow soils at a rates of 665 lbs and 792 lbs a.i/acre through chisel injection followed by tarping for 48 hours. The calculated field dissipation half-lives was less than 33.4hours. Volatilization of chloropicrin from applied fields may have resulted in short half-lives in the field dissipation study. Concentrations of chloropicrin at the 24-, 36-, and 48-inch depths increased to a maxima of 593.0, 230.5, and 75.2 ppm, respectively; times of maximum concentration were 12, 24, and 48 hours, respectively, after removal of the tarp.

The high Henry's Law Constant (2.05 X 10^{-3} atm M^3/mole) and rapid photohydrolysis of chloropicrin suggest that volatilization and rapid degradation are the primary environmental routes of dissipation from surface water. The calculated half-life of 31.1 hours for in aqueous solution (pH 7) when irradiated with xenon light source forming carbon dioxide, chloride, nitrate and nitrite (MRID 42900201). In the absence of light, chloropicrin did not hydrolyzed in sterile aqueous buffered solution under acidic to alkaline pH (MRID 43022401).

Soil adsorption coefficient (K_{oc}) of chloropicrin cannot be estimated from the batch equilibrium study. Due to the rapid volatilization of chloropicrin, it is unlikely that an equilibrium of chloropicrin in the batch equilibrium will be reached. The K_{oc} of chloropicrin was estimated using the EPA's computer model PCKOCWIN v1.66 of EPISUITE. EPI's K_{oc} estimations are based on the Sabljic molecular connectivity method. The estimated K_{oc} of chloropicrin is 36.05 ml/g. Chloropicrin's high water solubility (1621 mg/L) and low K_{oc} of 36.05 ml/g suggest its high mobility in the environment. The high solubility and low soil absorption of chloropicrin can result in movement of it downward to groundwater with water infiltration under an intense rainfall or continuous irrigation right after chloropicrin application. A supplemental leaching study (MRID 44191301) demonstrated that chloropicrin was very mobile in all four soils.

(b) Fate and Transport in atmosphere

In a review of the environmental fate of chloropicrin, Kollman 1990, noted that chloropicrin was likely to have relatively short persistence in the atmosphere. Chloropicrin was found to be susceptible to direct photolytic degradation in air. Laboratory simulation of exposure to artificial sunlight found that it degraded with a half-life of 20 days (MRID 05007865, Moilanen et al. 1978). However, a later study using a light source that better simulated the spectral intensity of sunlight found chloropicrin to photolyze much more rapidly, with an estimated atmospheric half-life of 3.4 to 8 hours in direct sunlight (Carter et al., 1997), leading to an estimate of 1 day for its atmospheric lifetime. The major degradation products were phosgene

(carbonyl chloride) and nitrosyl chloride, which rapidly photolyzes to reactive products NO and Cl• (Carter et al., 1997). Continued oxidation of the chloropicrin photolysis products would eventually produce CO_2, NO_2, N_2O_4, and Cl_2 (Ecotoxnet 2001). Phosgene has been detected in air downwind from a field application of chloropicrin (Woodrow et al. 1983), consistent with the results of laboratory photodegradation studies.

Although chloropicrin has significant aqueous solubility, its high vapor pressure results in limited partitioning into water; thus its Henry's Law Constant, 2.05×10^{-3} atm m^3/mol is comparable to that of long lived atmospheric vapors such as elemental mercury. Washout by rainfall would occur, but not at a rate likely to cause a significant reduction in the atmospheric half life of chloropicrin estimated from direct photodegradation. Similarly, uptake and subsequent degradation in soils and oceans would occur, but rates of these processes would likely be limited by atmospheric delivery to the soil or water interface, and hence approximate rates estimated for methyl bromide (Shorter et al. 1995, Yvon and Butler 1996).

An overall atmospheric lifetime for chloropicrin can be computed using the procedure followed by USEPA 2005b, in which an overall 'total lifetime' is computed from estimates of lifetimes computed from photodegradation, oceanic uptake and terrestrial uptake:

$$1/\tau_{total} = 1/\tau_p + 1/\tau_o + 1/\tau_s \qquad (1)$$

where τ_p, is the atmospheric lifetime associated with processes of direct and indirect photo and chemical degradation and precipitation scavenging; and τ_o ,and τ_s are lifetimes associated with uptake by oceanic and terrestrial surfaces, respectively.

The atmospheric lifetime of chloropicrin in the atmosphere was estimated to be 1 day (0.0027 years), based on the published photodegradation rate (Carter et al., 1997). If atmospheric lifetimes of 2.7 and 3.4 years are assumed for oceanic and terrestrial uptake and degradation processes (from methyl bromide), the estimate of atmospheric lifetime for chloropicrin remains 0.0027 years.

The highly toxic gas phosgene (once used as a chemical warfare agent) is a major photodegradation product of chloropicrin. Phosgene is resistant to both direct and indirect photochemical degradation processes in the atmosphere (Grosjean 1991; Helas and Wilson 1992), but it is extremely reactive with water, hydrolyzing rapidly to carbon dioxide and hydrochloric acid (Manoque and Pigford 1960). The dominant process removing phosgene from the atmosphere is its reaction with liquid water droplets (fog, clouds, and rain), with a tropospheric lifetime estimated at 10 hours to 1 day (Manoque and Pigford 1960). Despite its short atmospheric half life, phosgene has been commonly detected in air, especially in urban/industrial areas, with typical concentrations of 80 to 130 ng/m3 (WHO 1998). Phosgene is a widely used precursor in the chemical industry, with 3×10^6 metric tons produced and used annually (WHO 1998). Phosgene is also formed in the atmosphere by the photochemical oxidation of chloroethylenes, with generation rates estimated to be 350,000 metric tons annually (Singh 1976). Phosgene generation by conversion of 100% of chloropicrin used agriculturally in the U.S. would amount to about 6000 metric tons annually (based on U.S usage of 9000 metric

tons/year (NASS 2005). Even with such unrealistic conversion assumptions, chloropicrin usage appear to be a minor source of atmospheric phosgene relative to other sources.

Nitrosyl chloride is also produced in the photolysis of chloropicrin. This highly toxic gas is both photoreactive and readily hydrolyzed, and is estimated to have an atmospheric lifetime of less than 1 hour (Scheer et al. 1997).

The reactive byproducts of chloropicrin photolysis, in particular chlorine free radicals and NO_x, could lead to the generation of tropospheric ozone, although its potential (on a per molecule basis) for contributing to the generation of ozone in polluted urban atmospheres is no greater than the typical organic air pollutants contributing to the problem (Carter et al., 1997).

(c) Ozone Depletion Potential

The United Nations Industrial Development Organization listed chloropicrin as a non-ozone depleting alternative fumigant (UNIDO 2003). The ozone depletion potential (ODP) of methyl bromide was calculated by USEPA (USEPA, 2005) as 0.38 using an approach published in WMO 2002. In that approach, ODP is estimated by:

$$ODP(x) = FRF*\alpha*\tau_x/\tau_{CFC\text{-}11}*M_{CFC\text{-}11}/M_x*n_x/3 \qquad (2)$$

where FRF is the fractional release factor that describes the availability of a halogen for release from substance x relative to CFC-11, alpha is the efficacy of a halogen relative to chlorine at ozone destruction, and τ is the atmospheric lifetime or turnover time, M is molecular weight, and n_x is the number of halogen in a molecule of x. Using the FRF for methyl bromide (Agency was unable to find a value for chloropicrin), the ODP for chloropicrin is calculated as:

$$ODP_{(chloropicrin)} = [1.12*1*(0.0027/45)*137.7]/[164.4*(3/3)] \quad (3)$$
$$= 5.6*10^{-5}$$

With an ozone depletion potential more than four orders of magnitude ($5.6*10^{-5}$ versus 0.38) less than methyl bromide, stratospheric ozone depletion will not be a concern with the use of chloropicrin as a fumigant.

2. Measures of Terrestrial Exposure

(a)Terrestrial Exposure Modeling

To determine terrestrial exposure of chloropicrin, a deterministic approach was used in estimating exposures around the treated fields. This deterministic approach is based on monitoring data of chloropicrin and the use of the EPA's Industrial Source Complex: Short-Term Model (ISCST3) air dispersion model developed by USEPA (U.S.EPA, 1995). ISCST3 is a steady-state Gaussian plume model, which can be used to assess pollutant concentrations from a

wide variety of sources. The ISCST3 model is a publically vetted tool that is currently used by the Agency's Office of Air for regulatory decision making. A number of support documents for this tool can be found at the Agency's website *Technology Transfer Network Support Center for Regulatory Air Models* (http://www.epa.gov/scram001/tt22.htm#isc.) The ISCST3 has been used successfully to simulate fumigant levels in air following the fumigation of warehouses and agricultural fields located in California (Barry et al. 1997). ISCST3 provides useful results because it allows estimation of air concentrations based on changing factors such as application rates, field sizes, downwind distances, wind and weather conditions, and other factors. Using this model for the soil fumigants allows EPA to predict off-site movement given fixed meteorological and other conditions.

The modeling approaches used by the Agency were based on 24 hours exposure intervals (i.e., 24 hours time-weighted average of monitored air concentration of chloropicrin). Field sizes includes 1-, 5-, 10-, 20-, and 40 acre squares to represent a cross section of the fields that might be fumigated for agriculture use. ISCST3 was used in estimating air concentration using field emission ratio (ratio of the flux rate to the application rate), various sized fields, methods of chloropicrin placement, and different meteorological conditions. The basic approaches to estimate air concentrations using ISCST3 model are outlined in the Health Effects Division's Draft Standard Operating Procedures (SOPs) for Estimating Bystander Risk from Inhalation Exposure to Soil Fumigant (USEPA,2004). ISCST3 estimated downwind air concentrations using hourly meteorological conditions that include the wind speed and atmospheric stability.

In this assessment, one set of computations was completed using ISCST3 model at varying acreage and atmospheric conditions. The lower the wind speed and more stable the atmospheric environment, the higher the air concentrations were observed near the treated areas. The outputs were then scaled to appropriate emission ratios and application rates assuming stable weather condition, Table 5 reflects a wide variety of application rates and methods as well as the estimated concentrations of chloropicrin in air at the edge of a 40 acres field size under stable weather condition. The estimated maximum concentration of 0.019 mg/L (19037 mg/m^3) was used in calculating inhalation exposure for terrestrial organisms. California fumigant Permit conditions and detailed input assumptions and model results were described in the HED's Draft Chapter on Non-Occupational Risks Associated with Chloropicrin (USEPA, 2005c).

The specific inputs for the ISCST3 model calculations drove the associated uncertainties in the results. For example, the key input factors for pre-plant agricultural uses were field size, flux/emission rates, atmospheric stability, and windspeed. Wind direction is another factor which also should be considered. The field sizes used by the Agency in this assessment were 1 to 40 acres which is well within the range of what could be treated on a daily basis. There are uncertainties associated with point estimates of flux/emission rates for specific application techniques which is another varying factor. The flux rates which were used have been calculated by the Agency and they compare reasonably well with those calculated by the study investigators. The reality is that there is a large distribution of flux rates which is a phenomena inherent in the nature of these types of data.

Table 5. ISCTS3 estimated air concentrations of chloropicrin at various distances from the edge of 40 acres fumigated fields (meter) under several application methods

Application Methods	Tarping	Application Rate (lbs/Acre)	Concentraton Chloropicrin in Air (⌈g/m^3)			
			0 M*	25 M	50 M	100 M
Shank Injection Broadcast	Yes	350	19037	10951	8915	6876
Shank Injection Broadcast	No	175	15864	9126	7429	5730
Shank Injection Raised Bed	Yes	350	11319	6511	5301	4088
Shank Injection Raised Bed	No	175	11491	6610	5381	4150
Drip Irrigation	Yes	300	4373	2515	2048	1580

* Distances (meter) from the edge of the field

The values used for this assessment yield conservative air concentration estimates because considering a constant flux rate does not allow for diurnal/nocturnal changes that may occur, which when coupled with the appropriate wind speed and stability category, can result in lower concentrations. The meteorological inputs also will provide a conservative estimate of exposure because the wind direction is considered to be perpendicular (pointed downwind) to the treated field for the entire 24 hours represented in the calculation. This is not a normal situation in the atmosphere for most locations. There is normally a prevailing wind with directional changes over the course of a typical day, especially when diurnal and nocturnal differences are noted. Overall, Agency believes that the approach used to evaluate potential exposures from a known area source can be considered conservative. It is believed, however, that the range of selected input values and outputs represent what could reasonably occur in agriculture given proper field and climatological conditions.

(b) Terrestrial Exposure Monitoring Data

The short atmospheric lifetime indicate that readily detectable concentrations of chloropicrin should not accumulate in the atmosphere. A rough estimate of the steady-state tropospheric concentration that would be attained for release of 9000 metric tons/year (US annual usage in 2002, (NASS 2005)) to the atmosphere can be calculated by:

Input = Removal

$$= (1/\tau_{chloropicrin})*\text{volume of troposphere}*\text{steady state } [\text{chloropicrin}]_{air} \quad (4)$$

rearranged to:Steady State $[chloropicrin]_{air}$ = Input(moles/y)/ (volume of troposphere(1.6×10^{20} moles)*1/$\tau_{chloropicrin}$) and yielding:

Steady State $[chloropicrin]_{air} = 5.5X10^{7}$ moles/y/($1.6x10^{20}$ moles*1/0.0027 y)

$= 9.28 \times 10^{-16}$ mole fraction

$= 9.28 \times 10^{-4}$ ppt

$=6.24 \times 10^{-3}$ ng/m^3

If much of chloropicrin added to soils is degraded within the soil and not volatilized, an even lower steady state concentration would be expected.

Background concentrations (concentrations in air at sites remote from areas of recent application) of chloropicrin in air were below the analytical detection limit (30 ng/m^3) based on upwind or off target monitoring by the California Air Resources Board (CARB 2004, 2003). Thus, as predicted by its short atmospheric half life, the detection and measurement of chloropicrin in air is largely a local phenomenon. Measured concentrations would be expected to vary greatly with time and distance from areas of application, and with size and application rates of the areas receiving treatment.

In monitoring conducted in urban and rural communities near agricultural sites where chloropicrin was being applied in Monterey and Santa Cruz Counties, the California Air Resources Board observed concentrations of chloropicrin to range from undetected (<30 ng/m^3) to 14000 ng/m^3, with a range of 8-week average concentrations of 406 to 2270 ng/m^3. Chloropicrin was undetected in only 7 of 192 samples (CARB 2004). Similar monitoring in Kern County found much lower levels of chloropicrin (<30 - 750 ng/m^3, 8-week averages ranging from <30 - 42 ng/m^3), but chloropicrin was not being used extensively during the season at that location (CARB 2004). Most of the samples collected (185 of 198) were below the detection limit (<30 ng/m3). An assessment of chloropicrin risks to residents in rural communities estimated a mean 24 hour concentration of 210 ng/m^3 for residents during periods of chloropicrin application to nearby agricultural areas (Lee et al. 2002). Ambient chloropicrin concentrations are presented in **Table 6**.

Table 6. Ambient air concentrations of chloropicrin near fumigated fields.

Concentration (ng/m^3)	Exposure Type	Location	Date	Reference
210 ± 590 <85 - 4600	Rural residential	Kern Co., CA	1996	Lee et al. 2002

Table 6. Ambient air concentrations of chloropicrin near fumigated fields.

Concentration (ng/m^3)	Exposure Type	Location	Date	Reference
<85	Urban residential	Kern Co., CA	1996	Lee et al. 2002
<30 -14,000 daily, 8 week average = 406 - 2270	Rural residential	Monterey, Santa Cruz Co., CA	2001	CARB 2004
<30 - 3,300 daily, 8 week average = 660	Urban residential	Monterey, Santa Cruz Co., CA	2001	CARB 2004
<30 - 750, 8 week average = <40	Rural residential	Kern Co., CA	2001	CARB 2003

3. Measures of Aquatic Exposure

a. Aquatic Exposure Modeling

Henry's Law constant (2.05^{-3} atm-m^3/mol) of chloropicrin suggest that rapid volatilization of chloropicrin from water and soil surfaces is expected to be an important process. Since Tier I model GENEEC is not capable in accounting the loss of the vapor phase of chloropicrin from the fumigated field, Tier II PRZM/EXAMS was used in estimating chloropicrin concentrations in surface water. Additional chemical specific physical parameters vapor phase diffusion coefficient (DAIR) and enthalpy of vaporization (ENPY) were activated during the PRZM/EXAMS simulation. Intended application methods via shank or drip irrigation are to fumigate subsurface uniformly. Therefore, chemical application method (CAM) of 8 was used in mimicking subsurface fumigation of chloropicrin to simulate its uniform distribution within 25 cm through vapor diffusion under the tarp. Six field scenarios - California tomatoes, California onion, Florida strawberries, Florida tomato, North Carolina tobacco and North Carolina sweet potato were used in estimating EECs using highest application rate of 350 lbs/Acre. Chloropicrin uses in major crops like tomato, strawberries and tobacco as well as minor crops like onion and sweet potato scenarios were used in simulating PRZM/EXAMS to capture aquatic exposure under diverse crop scenarios.

Estimated environmental concentrations (EEC) of chloropicrin in surface waters were calculated using PRZM v.3.12 (Pesticide Root Zone Model), which simulates runoff and erosion from the agricultural field, and EXAMS v.2.98 (Exposure Analysis Modeling System), which simulates environmental fate and transport in surface water. A graphical user interface developed by EPA (http://www.epa.gov/oppefed1/models/water/) was employed to enter the

input values for each model run. A Mississippi pond scenario was used to determine estimated environmental concentrations (EEC) for ecological risk assessment. Each described a generic scenario for the EXAMS portion of the modeling exercise. Important input parameters used for the PRZM/EXAMS modeling are shown in Table 7.

Table 7. PRZM/EXAM Input Parameters for Chloropicrin

Parameters	Values & Units	Sources
Molecular Weight	164.39 g $Mole^{-1}$	MRID 43613901
Vapor Pressure 25°C	23.8 mm Hg	Merck Index
Water Solubility @ pH 7.0 and 25°C	1621 mg L^{-1}	MRID 43613901
DAIR	4858.6 cm^2/day	Fuller et al., 1966
ENPY	9.39 kcal/mole (39.3 kj/mol)	Chickos and Acree, 2003
Henry's Law Constant @ 25°C	2.05 X 10^{-3} atm M^3/mole	Kawamoto and Urano, 1989
Hydrolysis Half-Life (pH 7)	Stable	MRID 43022401
Aerobic Soil Metabolism $t_{½}$,	15.71 days	Calculated 90th Percentile MRID#s 43613901 Wilhelm et al., 1996
Aerobic Aquatic metabolism:	31.42 Days**	EFED Guideline
Anaerobic Aquatic metabolism: for entire sediment/water system	0.05 Days	MRID 43759301
Aqueous Photolysis	1.3 Day	MRID#s 42900201
Soil Water Partition Coefficient	36.05 L Kg^{-1}	EPISUITE
Pesticide is Wetted-In	No	Product Label
Crop Management		
Application rates (lb a.i./A) and Frequency	350 and 1X	Shank injection***
Fumigation Date for Florida and California Fumigation Date for North Carolina	September 15 April 15	USDA
Application Method	Ground Application (CAM 8)***	Standard assumption
Application Efficiency	100%	Standard assumption

Table 7. PRZM/EXAM Input Parameters for Chloropicrin

Parameters	Values & Units	Sources

* In absence of aerobic aquatic metabolism half-life, the reported half-lives of aerobic soil metabolism multiplied by 2 according to Guidance for selecting input parameters in modeling for environmental fate and transport of pesticides. Version II. December 4, 2001.
** The EPI (Estimation Program Interface) Suite is a Windows® based suite of physical/chemical property and environmental fate estimation models developed by the EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation SRC. http://www.epa.gov/opptintr/exposure/docs/updates_episuite_v3.11.htm
*** = Chemical Application method 8 using shank Injection to assume uniform distribution of chloropicrin within upper 25 cm soil depth

There are is an uncertainty in estimating chloropicrin exposure in water bodies due to post-application tarping of the treated area. If tarping is used to minimize the volatilization of chloropicrin, the loading of the chemical through runoff will be limited until the tarp is sliced or removed from the field. The present version of PRZM model and selected crop scenarios have limited capabilities in capturing the load of applied chemical under a post-application tarp scenario. PRZM also has limited capabilities in capturing the partitions of volatile chemical in air, water and sediment. Therefore, the estimated concentrations of chloropicrin in water bodies may be upper bound since the load of chloropicrin from runoff is considered in the PRZM/EXAMS simulation.

Table 8: Estimated Environmental Concentrations* (EECs) of Chloropicrin in surface water for selected crop scenarios

Crops	Application rate frequency	Acute: Peak EEC µg/L	Chronic 21-day Avg. EEC µg/L	Chronic 60-day Avg. EEC µg/L)
California Tomato	350 lbs a.i./Acre 1X Per Season	3.66	1.42	0.61
California Onion	350 lbs a.i./A 1X Per Season	2.14	0.61	0.24
Florida Tomato	350 lbs a.i./Acre 1X Per Season	107.8	30.7	12.48
Florida Strawberry	350 lbs a.i./Acre 1X Per Season	59.75	17.65	6.69
North Carolina Sweet Potato	350 lbs a.i./Acre 1X Per Season	1.67	0.48	0.18
North Carolina Tobacco	350 lbs a.i./Acre 1X Per Season	1.45	0.46	0.18

[a] Based on 1-in-10 year exceedance probability (0.10).

Results of the 1-in-10 year probabilities are summarized in **Table 8** and the full set of EECs are given in Appendix B.1.1 to B3.2. In addition, the method for calculating a 1-in-10 year EEC is described in Appendix B. The EECs presented in **Table 8** were used in this ecological risk assessment.

The important output parameters for the modeling exercises are the peak, 21 day, and 60 day chloropicrin levels estimated in the model pond. The highest EECs were observed for the Florida tomatoes and Florida strawberries scenarios. The large variation of chloropicrin levels estimated in surface waters can be traced to chemical loadings into the environmental pond from the PRZM output. Since the chemical input parameters are identical in each PRZM run, the different outputs are entirely dependent upon the different soil parameters used in the corresponding crop scenarios during the PRZM portion of the modeling exercise, as well as the scenario-specific meteorological data. A much higher percentage of pesticide was leached below the root zone level for the North Carolina and California scenarios as compared to the Florida scenarios due to a number of factors such as slope, soil type, moisture content, and the runoff curve numbers used for the different fields. This resulted in runoff and erosion flux vectors for the North Carolina and California scenarios were considerably lower than those estimated from the Florida tomatoes and Florida strawberries scenarios. As a consequence, the chloropicrin loadings into the EXAMS model environment were much lower, resulting in the smaller EECs.

b. Aquatic Exposure Monitoring and Field Data

Rapid volatilization of chloropicrin from water and soil surfaces is expected to be an important route of dissipation from the environment. Photolytic degradation of chloropicrin in water is also an important route of dissipation. Since this compound is very soluble in water and has low adsorption into soil, it can potentially leach into shallow ground water and leaky aquifers, as well as, may transport to nearby surface water through runoff and erosion, especially if chloropicrin application coincides with, or is followed soon by a rain event. Chloropicrin has been detected in the non-targeted monitoring wells. Based on the data base of pesticides in groundwater (U.S. EPA, 1992), chloropicrin was found at less than 1.00 μg/L in three wells from 15,175 wells in Florida.

C. Ecological Effects Characterization

Effects characterization describes the potential effects a pesticide can produce in an aquatic or terrestrial organism. This characterization is typically based on studies that describe acute and chronic effects toxicity information for various aquatic and terrestrial animals and plants. However, data for chloropicrin, while relatively extensive for mammals, are very limited otherwise. Appendix C summarizes the results of the toxicity studies used to characterize effects for this risk assessment. Toxicity testing reported in this section does not represent all species of

birds, mammals, or aquatic organisms. Only a few surrogate species for both freshwater fish and birds are used to represent all freshwater fish (2000+) and bird (680+) species in the United States. For mammals, acute studies are usually limited to Norway rat or the house mouse. Estuarine/marine testing is usually limited to a crustacean, a mollusk, and a fish. Also, neither reptiles nor amphibians are tested. The risk assessment assumes that avian and reptilian toxicities are similar. The same assumption is used for fish and amphibians.

In general, categories of acute toxicity ranging from "practically nontoxic" to "very highly toxic" have been established for aquatic organisms (based on LC_{50} values), terrestrial organisms (based on LD_{50} values), avian species (based on LC_{50} values), and non-target insects (based on LD_{50} values for honey bees) (EPA 2001). These categories are presented in Appendix C.

1. Aquatic Effects Characterization

a. Aquatic Animals

The most sensitive acute toxicity references values associated with chloropicrin exposure to aquatic organisms are summarized in **Table 9.** No chronic data are available. A more detailed summary of the available aquatic toxicity data is given in Appendix C.

Table 9. Chloropicrin toxicity reference values (TRVs) (ppb of active ingredient) for aquatic organisms.

Exposure Scenario	Species	Exposure Duration	Toxicity Reference Value (ppb a.i.)	Reference
Freshwater Fish				
Acute	Rainbow trout	48/96 hours	LC_{50} < 16.98 ppb (very highly toxic)	FTLR 425 Supplemental Study
Chronic	NA	NA	NA	NA
Freshwater Invertebrates				
Acute	*Daphnia pulex*	48 hours	LC_{50} <71 ppb (very highly toxic)	MRID 130704 Supplemental Study
Chronic	NA	NA	NA	NA

Table 9. Chloropicrin toxicity reference values (TRVs) (ppb of active ingredient) for aquatic organisms.

Exposure Scenario	Species	Exposure Duration	Toxicity Reference Value (ppb a.i.)	Reference
Estuarine/Marine Fish				
Acute	NA	NA	NA	NA
Chronic	NA	NA	NA	NA
Estuarine/Marine Invertebrates				
Acute	NA	NA	NA	NA
Chronic	NA	NA	NA	NA
Aquatic Plants				
Acute	NA	NA	NA	NA

NA = Data appropriate for quantitative use are not available.

Acute Toxicity to Freshwater Fish

The acute toxicity of chloropicrin to freshwater fish was evaluated in rainbow trout and bluegill sunfish, with LC_{50}s of < 16.98 ppb (very highly toxic) and < 105 ppb (at least highly toxic), respectively. The values are expressed as "less than" the numeric value, since chloropicrin is highly volatile and measured residues were not provided. The rainbow trout value is used as the toxicity value for assessing acute risks to fish from exposure to chloropicrin.

Acute Toxicity to Freshwater Invertebrates

The acute toxicity of chloropicrin to aquatic invertebrates has been assessed in *Daphnia pulex*, with a 48-hour LC_{50} value of < 71 ppb (very highly toxic). The value is expressed as "less than" the numeric value, since chloropicrin is highly volatile and measured residues were below the Level of Quantitation at the lowest four test levels at 48 hours. Although residues were below the Level of Quantitiation, 10 - 20% mortality of daphnids occurred at these test levels.

2. Terrestrial Effects Characterization

a. Terrestrial Animals

The toxicity endpoints used to characterize risks of chloropicrin exposure to birds and mammals are summarized in **Table 10.** Results of all studies in terrestrial animal species are summarized in Appendix C.

Table 10. Toxicity reference values (TRVs) for terrestrial species for chloropicrin.

Exposure Scenario	Species	Exposure Duration	Toxicity Reference Value[1]	Reference
Mammals				
Acute oral	Rat	Single oral dose	LD_{50} = 37.5 mg/kg (highly toxic)	MRID 05014376 Acceptable/Guide-line
Acute inhalation	Rat	4-hour inhalation	LC_{50} = 17 ppm (M) and 19 ppm (F) [conv. to mg/L: Section IV.B.2]	MRID 45117902 Acceptable/Non-guideline
Chronic inhalation	Rabbit	6 hrs./day on days 7 - 29 (inhalation)	NOAEL = 0.4 ppm (0.003 mg/L)	MRID 42740601 Acceptable/ guideline
Birds				
Acute	No Data			
Chronic	No Data			

[1]Data from 9/30/04 and 1/31/05 HED Chloropicrin Assessments.

Mammalian Species

Based on the above results of an acute oral toxicity study in rats, EFED considers chloropicrin to be highly toxic to mammals. The acute oral value is used in this risk assessment only for the LD50 per square foot preliminary analysis. The acute inhalation and chronic inhalation endpoints are used for the inhalation analyses.

IV. Risk Characterization

A. Risk Estimation - Integration of Exposure and Effects Data

1. Non-target Aquatic Animals and Plants

There are uncertainties in estimating chloropicrin exposure in surface water from post-application, due to tarping of the treated area. If tarping is used to minimize the volatilization of chloropicrin, the loading of the chemical through runoff will be limited until the tarp is sliced or removed from the field. The present version of the PRZM model, as well as the selected crop scenarios, has limited capabilities in discounting the load from runoff of applied chemical under a post-application tarp scenario. Since the load of chloropicrin from runoff is considered in the PRZM/EXAMS simulation, the estimated concentrations of chloropicrin in surface water bodies may be upper bound. Therefore, PRZM/EXAMS estimated exposure values may contribute upper bound LOCs for the aquatic organisms.

Risk quotients for aquatic animals are presented in **Table 11**. The risk quotients are calculated using the toxicity values summarized in **Table 9** and EECs from PRZM/EXAMS summarized in **Table 8**. For assessing acute risks, the 24-hour peak concentration is used. Chronic toxicity data are not available to calculated chronic risk quotients.

Table 11. Risk Quotients (RQs) for chloropicrin for acute exposures of aquatic species.

Exposure Scenario	Exposure (ppb)	Toxicity Reference Value (ppb)	Risk Quotient[1]
Freshwater Fish			
Acute risk[2]			
California tomato	3.66	<16.98	>0.22**
California onion	2.14	<16.98	>0.12**
Florida tomato	107.80	<16.98	>6.35***
Florida strawberry	59.75	<16.98	>3.52***
North Carolina sweet potato	1.67	<16.98	>0.10**
North Carolina tobacco	1.45	<16.98	>0.09*
Freshwater Aquatic Invertebrates			

Table 11. Risk Quotients (RQs) for chloropicrin for acute exposures of aquatic species.

Exposure Scenario	Exposure (ppb)	Toxicity Reference Value (ppb)	Risk Quotient[1]
Acute risk[4]			
California tomato	3.66	<71	>0.05*
California onion	2.14	<71	>0.03
Florida tomato	107.80	<71	>1.52***
Florida strawberry	59.75	<71	>0.84***
North Carolina sweet potato	1.67	<71	>0.02
North Carolina tobacco	1.45	<71	>0.02

*Exceeds acute endangered species LOC (≥ 0.05)
**Exceeds acute endangered species LOC and acute restricted use LOC (≥ 0.1)
***Exceeds acute endangered species LOC, acute restricted use LOC, and acute risk LOC (≥ 0.5)

Freshwater Fish and Invertebrates

As shown by the asterisks in the table above, all six of the scenarios exceed at least one acute LOC, for fish and/or aquatic invertebrates (based just on the numeric portion of the risk quotients shown). Given that all risk quotients are expressed as "greater than" these numeric values, all scenarios for both taxonomic groups could potentially exceed LOCs. Whether or not they do will depend on future resolution of definitive toxicity values.

Specifically, for freshwater fish, risk quotients exceed a) the endangered species acute LOC (0.05) for all six scenarios, b) the restricted use LOC (0.1) for all scenarios except North Carolina tobacco, and c) the acute risk LOC (0.5) for Florida tomatoes and Florida strawberries. For aquatic invertebrates, risk quotients exceed a) the endangered species acute LOC (0.05) for California tomatoes, Florida tomatoes, and Florida strawberries, and b) the restricted use LOC (0.1) and the acute risk LOC (0.5) for Florida tomatoes and Florida strawberries.

2. Non-target Terrestrial Animals

a. Risk to Mammals

EFED has used the established LD50/square foot risk assessment method for mammals as a risk calculation screen. This method is considered to cover all routes of exposure, although it

uses an acute oral toxicity value. It is typically used for granular and similar products, but it is considered acceptable for use as a screen for chloropicrin. Uncertainties of the method, in general, include 1) non-oral routes of exposure may be either more or less hazardous than the oral route, and 2) an organism would not typically take up all the toxicant from any given square foot, and the amount of toxicant in this unit of area may be more or less than that which an organism receives overall as a dose. For evaluating exposure to a highly volatile chemical applied below ground, there is added uncertainty since all the chemical applied is not available at the surface at any one time, for example. It's value for the present assessment is as a preliminary screen to confirm whether a refined route-specific (e.g., inhalation) analysis is appropriate. That is, the LD50/square foot calculations reflect all routes of exposure. One then looks more closely at the individual routes of exposure that are most appropriate (i.e., inhalation for fumigants) (E. Odenkirchen, personal communication).

At 350 lb ai/A of chloropicrin, there would be 3,645 mg ai/square foot (given 43,560 square feet/A and 453,590 mg/lb). This exposure amount is divided by the product of acute oral LD50 for mammals (37.5 mg/kg) and body weight of mammal (in kg) to calculate risk quotients. Three mammal body weights are assessed: 15 g, 35 g, and 1000 g. The resulting risk quotients (LD50s/sq. ft.) for these three sizes of mammals are 6,480; 2,777; and 97, respectively. These far exceed the acute risk LOC of 0.5, as well as the acute restricted use LOC of 0.2 and the acute endangered species LOC of 0.1. Thus, this preliminary screen indicates a potential for concern for risk to wild mammals, and a need for further analysis.

The main route of wild mammal exposure is likely to be from inhalation of chloropicrin off-gassing from treated fields. Mammalian inhalation toxicity data are available. However, EFED does not currently have established LOCs based on inhalation exposure. Nevertheless, an inhalation risk concern for wild mammals has been identified. See the Risk Description for the more refined assessment of risk based on inhalation exposure.

b. Risk to Avian Species

The main route of exposure of birds is likely to be from inhalation of chloropicrin off-gassing from treated fields. However, avian inhalation data are not available. EFED has used the established LD50/square foot method for mammals as a rough risk calculation screen (see above). However, this screen has not been done for birds since the necessary acute oral value for birds with chloropicrin is not available. See the Risk Description for analysis of inhalation risk to mammals and how this relates to potential risk to birds.

3. Non-target Terrestrial and Semi-aquatic Plants

Plant toxicity data [123-1(a), 123-1(b)] are needed for risk assessment because of the potential for exposure and risk to exposed terrestrial and semi-aquatic plants off-site.

B. Risk Description

1. Risk to Aquatic Organisms

A. Animals

Chloropicrin has the potential to reach surface water bodies. EECs to determine the acute and chronic risk to aquatic organisms were estimated using PRZM/EXAMS models with selected scenarios (CA tomatoes, CA onions, FL tomatoes, FL strawberries, NC sweet potatoes, NC tobacco), to represent the numerous crops for which chloropicrin is registered for use. Although the same application rate of 350 lbs ai/A was used for all scenarios, the chloropicrin exposure estimated resulted in different risk potentials, due to the different conditions (e.g., rainfall, soil temperature) for each modeled location. Also, for a given amount of chloropicrin transported to a water body, there is expected to be greater aquatic organism exposure in colder waters, since the Henry's Law Constant will be lower in colder waters, resulting in lower volatilization (and conversely, lower exposure in warmer waters).

Based on this exposure assessment: for fish, risk quotients are considered to exceed a) the endangered species acute LOC (0.05) for all six scenarios, b) the restricted use LOC (0.1) for all scenarios except North Carolina tobacco, and c) the acute risk LOC (0.5) for Florida tomatoes and Florida strawberries. For aquatic invertebrates, risk quotients are considered to exceed a) the endangered species acute LOC (0.05) for California tomatoes, Florida tomatoes, and Florida strawberries, and b) the restricted use LOC (0.1) and the acute risk LOC (0.5) for Florida tomatoes and Florida strawberries. In these cases, the LOCs are exceeded based just on the numeric value of the risk quotients. As explained earlier, given that all risk quotients are expressed as "greater than" these numeric values, all scenarios for both taxonomic groups could potentially exceed LOCs. Whether or not they do will depend on future resolution of definitive toxicity values. Also, only a select number of use sites have been modeled, and it is likely that other use sites would have aquatic exposures in the range of those sites modeled. Thus, it cannot be determined that any use site does not exceed acute LOCs. However, in addition to the uncertainty concerning the toxicity of chloropicrin to aquatic animals (i.e., chloropicrin is apparently more toxic than indicated in the studies), there are also substantial uncertainties concerning exposure modeling values, as described earlier.

In addition to the toxicity values used for risk quotients, a literature search value for the mysid shrimp (257.8 ppb) was located via ECOTOX (Carr, 1987). However, this reported value was based on a static test without measured concentrations, unlike the submitted and reviewed daphnid study where some measured concentrations were available. Also, the reported mysid

value is higher (i.e., implying lower toxicity) than that available daphnid study (although with no confirmation of residues at all in the mysid study, it is not possible to confirm what the toxicity is). It is thus not used quantitatively in this screening assessment.

B. Plants

Aquatic plant toxicity data (123-2) are needed for risk assessment because of the potential for exposure and risk to aquatic plants off-site.

2. Risk to Terrestrial Organisms

A. Animals

EFED's major concern with chloropicrin in the terrestrial environment is that it is highly volatile and can off-gas from treated fields and potentially expose a range of nontarget terrestrial organisms in its path. Given the broad spectrum use of chloropicrin, it is assumed that most living organisms in the treated fields (including any beneficial insects and/or burrowing mammals) would be at high risk of mortality.

EFED used the screening-level $LD50/ft^2$ method as a preliminary step to assess risks of the pesticide to mammals. This method has most frequently been applied to pesticide application scenarios involving granular formulations, seed treatments, and baits. The method has not been generally applied to situations involving highly volatile compounds, but remains the Agency's most appropriate index for this type of use. This $LD50/ft^2$ method is an index that does not systematically account for exposures from each potential route, but considers the overall potential for adverse effects given a bioavailable amount of pesticide conservatively related to the mass applied per unit area at the treatment site. See the uncertainty discussion in the Risk Estimation section above. Three mammal body weights are assessed: 15g, 35g, and 1000g. The resulting risk quotients for these three sizes of mammals are 1,897, 813, and 28, respectively (see the Risk Estimation section above). These far exceed the acute risk LOC of 0.5, as well as the acute restricted use LOC of 0.2 and the acute endangered species LOC of 0.1. Thus, this preliminary screen indicates a potential for concern for risk to wild mammals, and a refined analysis based specifically on inhalation exposure is described below.

Owing to the limitations of the the $LD50/ft^2$ method for highly volatile compounds and the recognized high potential volatility of chloropicrin, EFED investigated the potential for inhalation to be a toxicologically significant route of exposure to birds and mammals within the use area. While data on inhalation toxicity are available for mammals (from HED), inhalation toxicity data are not available for birds.

Available ambient monitoring data for chloropicrin indicates a maximum ambient air residue of 14,000 ng/m^3 (see **Table 6**). This is equivalent to a chloropicrin air concentration of 0.000014 mg/L. A comparison of this air concentration with available mammalian acute inhalation effects data (LC50 of 0.114 mg/L) would indicate a risk quotient of 0.00012, well below any LOC.

Monitoring data for a limited number of application sites is not necessarily predictive of all site conditions where the pesticide may be used. Also, most monitoring data is for samples collected at least 1.0 m above the ground, often higher. This height is above the level for many ground-dwelling mammals and ground-feeding birds. It is reasonable to assume a gradient of concentrations at the treatment site, with higher concentrations of chloropicrin occurring closer to the ground. This would be especially applicable to those times that a tarp is not used (and animals would be more likely to be on the soil surface of the treated field). Thus, modeling has been used to attempt to estimate residues closer to the field and ground.

The ISCST3 model provides more flexibility compared to the monitoring data (i.e., results are more easily extrapolated) and generally allows the Agency to consider a much broader set of circumstances in its assessments. Nevertheless, since EFED is relying on off-site monitoring data, the model calculation does not specifically produce on-field, ground surface level air residues. Because of uncertainties associated with both monitoring and modeling, the Agency has calculated risk estimates based on both, for comparison.

The ISCST3 model estimated concentrations were used in calculating the concentrations on the edge of the field from a field application of chloropicrin. The highest air concentration of 0.019 mg/L was estimated. With an acute mammal inhalation LC50 of 17 ppm (0.114 mg/L), the risk quotient for this modeled concentration is 0.17 (0.019 /0.114).

The Agency has not established level of concern (LOC) thresholds expressly for the interpretation of RQs calculated for inhalation exposure risks. However, if the existing LOC values for acute mammalian wildlife risk were used to evaluated such RQs, the above analysis based on modeling (risk quotient of 0.17) would suggest that at least some uses of chloropicrin could exceed the acute endangered species LOC (0.1), but not the acute restricted use LOC (0.2) or acute risk LOC (0.5). The uncertainty level in these analyses can be reduced with submission of ground-level monitoring data (e.g., 3 inches) both within-field and edge-of-field, for maximum application rates.

The above assessment is limited to acute effects and exposure windows. Wild mammals may have home ranges in the treatment area and may be exposed continuously and/or repeatedly as the result of chloropicrin use on multiple fields over multiple days in any geographic area. Given that the rabbit inhalation developmental toxicity NOAEL for chloropicrin is 0.003 mg/L (with the developmental LOAEL of 0.008 mg/L based on abortions and decreased fetal weights), lower than the acute inhalation endpoint, EFED investigated the potential for a concern for chronic exposure and effects. Given the short atmospheric half-life of chloropicrin described

earlier, it appears unlikely than long-term exposure would occur from any single application of chloropicrin. However, multiple fields may be treated in an area over a number of days. Therefore, there still exists a potential that mammals within an area of multiple treated fields may be exposed to chloropicrin emissions on a repeated basis over time. Comparison of the previously cited maximum ambient air residues (0.000014 mg/L) to the 0.003 mg/L NOAEL above implies that ambient air residues are likely to be well below developmental effect levels.

The above analysis is based on mammalian toxicity data for the inhalation route. A similar analysis could be performed for birds, if the necessary data were available. However, no inhalation toxicity data for chloropicrin are available for birds. If acute toxicity by the oral route were available for both mammals and birds, an evaluation of the relative sensitivity via the oral route might be extrapolated to the inhalation route to estimate an acute inhalation endpoint for birds. However, no acute oral LD50 data for chloropicrin are available for birds. Therefore, EFED is limited to an assumption of equivalent sensitivity between birds and mammals for exposure through inhalation. EFED feels that such an extrapolation may not be protective, given higher respiration rates for birds versus mammals, and physiological differences in the avian lung that would tend to favor higher diffusion rates across the lung membrane when compared to mammals. Therefore, inhalation analyses that suggest a potential for adverse effects in mammals would also suggest potential risks to birds via the inhalation route, but analyses not indicating risk to wild mammals would not necessarily be true for birds also.

Although birds are mobile and some may only have a very brief exposure flying by, others may have territories or nests in the area and be exposed more substantially and/or repeatedly (in addition, eggs are gas permeable and could be exposed). Repeat exposures can occur since chloropicrin may be applied to different fields in a given geographic area on different days. The uncertainty level can be reduced with this screening-level analysis by submission of avian acute inhalation toxicity data, in addition to the above-cited ground-level monitoring data. A laboratory subchronic/chronic avian inhalation study will help EFED address potential repeated exposure of birds over time in the wild.

B. Plants

Based on the phytotoxicity of chloropicrin on the treated fields, it is expected that non-target plants off-site may also be a risk from off-gassed chloropicrin. Terrestrial plant guideline toxicity data are needed to evaluate this risk.

3. Review of Incident Data

Extremely limited terrestrial animal (non-human) incident data are available for chloropicrin. For example, there was an incident in Europe, in which a mis-labeled product that was later determined to contain chloropicrin was inadvertently used in a greenhouse in combination with metam sodium. It resulted in large numbers of domestic animal deaths when the chloropicrin gas escaped to the surrounding area (Selala, et. al. 1989). Although this incident does <u>not</u> reflect the expected exposure from labeled uses reviewed in the present risk

assessment, it does indicate the potential for hazard if chloropicrin were to be mis-handled and get into the ground-level air at high concentrations.

In an aquatic animal incident involving chloropicrin and telone beginning 9/1/05, several thousand dead fish were reported over a 3-mile reach of Casserly Creek in Santa Cruz County, California. The mortality appeared to begin near a strawberry field being fumigated (using chemigation) with the product Inline (R). Species killed included steelhead/rainbow trout, sculpin, hitch, and Sacramento blackfish. Crayfish were also killed (I-016955-001; 11/18/05 Pesticide Laboratory Report, California Department of Fish and Game). Inline (R) (Registration number 62719-348) is a 60.8 % telone/33.3 % chloropicrin product. EFED is expected to assign a certainty level in the Ecological Incident Information System (EIIS) of "highly probable" for chloropicrin in this incident, based on the 11/18/05 report. The California Pesticide Investigations Unit is checking further as to how the pesticide moved to the stream. There is no mention of rain in the 11/18/05 report, the applicator has cited a possible defective valve in a flush line (I-016884), and the registrant has claimed that a valve was mistakenly opened (I-016738-016).

Also, fish farm incidents have shown the potential for another off-gassed fumigant, MITC (from agricultural application of metam-sodium) to be inadvertently drawn into man-made aeration systems, resulting in possible fish mortality. Based on the similar off-gassing potential of chloropicrin, this same risk may apply to this chemical, if it is applied to fields in the vicinity of fish farms with air intake systems. Chloropicrin is heavier than air and could potentially travel along the ground and be inadvertently drawn into such systems.

Three plant incidents involving fumigant products with chloropicrin as one of the active ingredients have been identified in a 1/19/06 report by M. Kathleen O'Malley (ITRMD/OPP). One of these involved the product Telone C-35 (62719-302; 63.4% telone, 34.7% chloropicrin) and was coded as major by ITRMD. The other two incidents were coded by ITRMD as minor: one involved this same combination product with telone; the other involved a combination product with methyl bromide (Tri-con 57/43 Preplant Soil Fumigant; 11220-4, 57% methyl bromide, 42.6% chloropicrin). These incidents help confirm the EFED assumption that chloropicrin has the potential to adversely affect non-target plants.

4. Endocrine Disruption

Chloropicrin does not appear to present a specific endocrine disruption risk at present. Nevertheless, EPA is required under the FFDCA, as amended by FQPA, to develop a screening program to determine whether certain substances (including all pesticide active and other ingredients) *"may have an effect in humans that is similar to an effect produced by a naturally occurring estrogen, or other such endocrine effects as the Administrator may designate."* Following the recommendations of its Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC), EPA determined that there was a scientific basis for including, as part of

the program, the androgen and thyroid hormone systems, in addition to the estrogen hormone system. EPA also adopted EDSTAC's recommendation that the Program include evaluations of potential effects in wildlife. For pesticide chemicals, EPA will use FIFRA authority, and, to the extent that effects in wildlife may help determine whether a substance may have an effect in humans, FFDCA authority, to require the wildlife evaluations. As the science develops and resources allow, screening of additional hormone systems may be added to the Endocrine Disruptor Screening Program (EDSP). When the appropriate screening and/or testing protocols being considered under the Agency's EDSP have been developed, chloropicrin may be subjected to additional screening and/or testing to better characterize effects related to endocrine disruption.

5. Federally Threatened and Endangered (Listed) Species Concerns

A. Action Area

For listed species assessment purposes, the action area is considered to be the area affected directly or indirectly by the Federal action and not merely the immediate area involved in the action. At the initial Level I screening assessment, broadly described taxonomic groups are considered and thus conservatively assumes that listed species within those broad groups are co-located with the pesticide treatment area. This means that terrestrial plants and wildlife are assumed to be located on or adjacent to the treated site, and aquatic organisms are assumed to be located in a surface water body adjacent to the treated site. The assessment also assumes that the listed species are located within an assumed area which has the relatively highest potential exposure to the pesticide, and that exposures are likely to decrease with distance from the treatment area. Section II. B of this risk assessment presents the pesticide use sites that are used to establish initial collocation of species with treatment areas.

If the assumptions associated with the screening-level action area result in RQs that are below the listed species LOCs, a "no effect" determination conclusion is made with respect to listed species in that taxa, and no further description of an action area is necessary. Furthermore, RQs below the listed species LOCs for a given taxonomic group indicate no concern for indirect effects upon listed species that depend upon the taxonomic group covered by the RQ as a resource.

However, in situations where the screening assumptions lead to RQs in excess of the listed species LOCs for a given taxonomic group, a potential for a "may affect" conclusion exists and may be associated with direct effects on listed species belonging to that taxonomic group or may extend to indirect effects upon listed species that depend upon that taxonomic group as a resource. In such cases, additional information on the biology of listed species, the locations of these species, fate and transport properties of the chemical, and the locations of use sites could be considered to determine the extent to which screening assumptions regarding an action area apply to a particular listed organism. These subsequent refinement steps could consider how this

information would impact the action area for a particular listed organism and may potentially include areas of exposure that are downwind and downstream of the pesticide use site.

B. Taxonomic Groups Potentially at Risk

The Level I screening assessment process for listed species uses the generic taxonomic group-based process to make inferences on direct effect concerns for listed species. The first iteration of reporting the results of the Level I screen is a listing of pesticide use sites and taxonomic groups for which RQ calculations reveal values that meet or exceed the listed species LOCs. In the majority of cases, the screening-level risk assessment process reports RQ calculations for the following broad taxonomic groupings:

- Birds (also used as surrogate for terrestrial-phase amphibians and reptiles)
- Mammals
- Freshwater fish (also used as a surrogate for aquatic phase amphibians)
- Freshwater invertebrates
- Estuarine/marine fish
- Estuarine/marine invertebrates
- Terrestrial plants
- Algae and aquatic plants

For chloropicrin, risk quotients could not be calculated for most of these, due to a lack of data. There may also be taxonomic groups of listed species for which screening tools are not fully developed nor represented through surrogacy with existing tools. For example, there is no RQ calculation process for terrestrial invertebrates. Since chloropicrin is used to kill certain terrestrial invertebrates, it must be assumed for a screening analysis that listed terrestrial invertebrates may be directly adversely affected as well.

1. Discussion of Risk Quotients

Endangered Species LOCs are exceeded for wild mammals, fish, and aquatic invertebrates based on acute risk quotients. Although guideline avian toxicity data are not available, birds may be as sensitive as mammals. The aquatic risk quotients are all indeterminate (>) since the toxicity values are indeterminate (<). Thus, while some modeled site risk quotients are clearly above endangered species LOCs (i.e., they are above the LOC even without the >), EFED cannot confirm that any site definitely does not exceed a fish or aquatic invertebrate LOC. Terrestrial invertebrates are target species and thus nontarget terrestrial invertebrates may also be at risk. Plants on treatment sites may be susceptible to chloropicrin and thus plants off-site may also be susceptible to off-gassed chloropicrin. Should estimated exposure levels occur in proximity to listed resources, the available screening level information suggests a potential

concern for direct acute effects on listed wild mammals, birds, fish, aquatic invertebrates, terrestrial invertebrates, and plants associated with soil fumigant sites.

2. Probit Dose Response Relationship

An analysis has been conducted of the probability of individual mortality at an LOC of 0.1, the acute endangered species LOC for wild mammals. It is recognized that extrapolation of very low probability events is associated with considerable uncertainty in the resulting estimates. The analysis uses the EFED spreadsheet IECv1.1.xls, developed by EFED (USEPA, 2004).

For mammals, slope and and confidence interval information for the slope were not reported in the Data Evaluation Record for MRID 45117902, an acute inhalation study. Risk quotients in the ecological risk assessment used the inhalation toxicity value for male rats, where there was only one partial mortality. Since probit results are not possible with only one partial mortality, a default slope of 4.5 and confidence interval of 2 to 9 are used for the individual mortality probability analysis. Based on an assumption of a probit dose response relationship with a mean estimated slope of 4.5, the corresponding estimated chance of individual mortality associated with the listed species LOC of 0.1, the acute toxic endpoint for wild mammals, is approximately one in 294,000. To explore possible bounds to such estimates, the upper and lower values for the mean slope estimate (2 - 9) were used to calculate upper and lower estimates of the effects probability associated with the listed species LOC. These values are approximately one in 44 and one in 10^{16} (default limit of Excel reporting).

As previously indicated, the acute risk quotient for mammals is estimated to be 0.14, based on modeling. This is slightly higher than the mammal acute endangered species LOC of 0.1. Thus, the probability of individual mortality at the predicted exposures used for the risk quotients would also be higher than at the LOC.

Data are not adequate to calculate individual effect probabilities for freshwater fish and aquatic invertebrates. This is due to a lack of measured concentrations in the fish studies and uncertainties in the measured concentrations in the daphnid study (in the lowest four concentrations at 48 hours). Data are not available to calculate individual effects for other taxonomic groups.

C. Data Related to Under-represented Taxa

Although the Level I screening assessment process relies on RQ calculations that use toxicity endpoints selected from the most sensitive species tested within broad taxonomic groups, there may be situations in which additional effects data from one or more sources may suggest that a given suite of listed taxa may be more or less sensitive than suggested by the effects data used for RQ calculations. In these circumstances, the screening level RQs are not changed, but effects data more specific to listed species may be used to evaluate the extent to which screening-level RQs adequately represent conclusions regarding effects on specific listed taxa. However, this does not appear to apply to chloropicrin.

D. Implications of Sublethal Effects

For mammals, adverse effects were seen in a variety of chronic inhalation studies. The endpoint selected for ecological risk assessment is the developmental NOAEC of 0.4 ppm in rabbits. Abortions and decreased fetal weights occurred at the LOAEL of 0.8 ppm in this study. Thus, it is expected that sublethal effects could be seen in listed mammals, if exposed at levels comparable to those producing effects in the lab.

E. Indirect Effects Analysis

The Agency acknowledges that pesticides have the potential to exert indirect effects upon the listed organisms by perturbing forage or prey availability or altering the extent and nature of nesting habitat, for example. In conducting a screen for indirect effects, the Agency uses the direct effects LOCs for each taxonomic group to make inferences concerning the potential for indirect effects upon listed species that rely upon non-endangered organisms in these taxonomic groups as resources critical to their life cycle.

For chloropicrin, direct effect LOCs are exceeded for mammals, fish and aquatic invertebrates, as indicated above. Birds may be as sensitive as mammals. Also, since chloropicrin is intended to kill certain target terrestrial invertebrates, it could also potentially have a direct effect on nontarget terrestrial invertebrates. It also has some phytotoxicity potential on treated sites, and thus, might also have some potential for phytotoxicity off-site. In addition to these potential direct effects, there may thus be a potential for indirect effects to those listed species that are dependent upon mammals, birds, fish, aquatic invertebrates, terrestrial invertebrates, and/or plants.

F. Critical Habitat

In the evaluation of pesticide effects on designated critical habitat, consideration is given to the physical and biological features (constituent elements) of a critical habitat identified by the U.S Fish and Wildlife and National Marine Fisheries Services as essential to the conservation of a listed species and which may require special management considerations or protection. The evaluation of impacts for a screening level pesticide risk assessment focuses on the biological features that are constituent elements and is accomplished using the screening-level taxonomic analysis (risk quotients, RQs) and listed species levels of concern (LOCs) that are used to evaluate direct and indirect effects to listed organisms.

The screening-level risk assessment has identified potential concerns for indirect effects on listed species for those organisms dependant upon mammals, birds, fish, aquatic invertebrates, terrestrial invertebrates, and/or plants. In light of the potential for indirect effects, the next step for EPA and the Service(s) is to identify which listed species and critical habitat are potentially implicated. Analytically, the identification of such species and critical habitat can occur in either

of two ways. First, the agencies could determine whether the action area overlaps critical habitat or the occupied range of any listed species. If so, EPA would examine whether the pesticide's potential impacts on non-endangered species would affect the listed species indirectly or directly affect a constituent element of the critical habitat. Alternatively, the agencies could determine which listed species depend on biological resources, or have constituent elements that fall into, the taxa that may be directly or indirectly impacted by the pesticide. Then EPA would determine whether use of the pesticide overlaps the critical habitat or the occupied range of those listed species. At present, the information reviewed by EPA does not permit use of either analytical approach to make a definitive identification of species that are potentially impacted indirectly or critical habitats that is potentially impacted directly by the use of the pesticide. EPA and the Service(s) are working together to conduct the necessary analysis.

This screening-level risk assessment for critical habitat provides a listing of potential biological features that, if they are constituent elements of one or more critical habitats, would be of potential concern. These correspond to the taxa identified above as being of potential concern for indirect effects and includes mammals, birds, fish, aquatic invertebrates, terrestrial invertebrates, and/or plants. This list should serve as an initial step in problem formulation for further assessment of critical habitat impacts outlined above, should additional work be necessary.

G. Co-occurrence Analysis

The goal of the analysis for co-location is to determine whether sites of pesticide use are geographically associated with known locations of listed species. At the screening level, this analysis is accomplished using the LOCATES database. The database uses location information for listed species at the county level and compares it to agricultural census data for crop production at the same county level of resolution. The product is a listing of federally listed species that are located within counties known to produce the crop upon which the pesticide will be used. Because the Level I screening assessment considers **both** direct and indirect effects across generic taxonomic groupings, it is not possible to exclude any taxonomic group from a LOCATES database run for a screening risk assessment.

Because chloropicrin is registered for preplant use on all “terrestrial food crops” (as well as ornamental and other sites), essentially all use sites from LOCATES would have to be selected. As indicated above, for a screen for both direct and indirect effects, all taxonomic groups would also have to be selected. Thus, a printout would essentially include all known federally-listed species for all taxonomic groups in all counties with agriculture. If the registrants are able to limit labels to a more narrow set of crops, a more narrow set of counties and species can be developed. If this is not done, the species-specific analysis will have to include virtually all known federally-listed species for all taxonomic groups in all counties with agriculture.

The registrants must provide information on the proximity of federally-listed mammals, birds, fish, aquatic invertebrates, terrestrial invertebrates, and plants to the registered use sites. This

requirement may be satisfied in one of three ways: 1) having membership in the FIFRA Endangered Species Task Force (Pesticide Registration [PR] Notice 2000-2); 2) citing FIFRA Endangered Species Task Force data; or 3) independently producing these data, provided the information is of sufficient quality to meet FIFRA requirements. The information will be used by the OPP Endangered Species Protection Program to develop recommendations to avoid adverse effects to listed species.

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VI. Appendices

Appendix A. Environmental Fate and Transport Data

161-1 Hydrolysis (MRID# 43022401)

Chloropicrin, at approximately 100 ppm, did not hydrolyze in sterile aqueous buffered solutions adjusted to pH 5, 7, and 9, that were incubated in the dark at 25□C.During the 28 day study, chloropicrin ranged from 106.4 to 113.8 ppm in the pH 5 acetate buffer solution, from 97.3 to 113.7 ppm in the pH 7 phosphate buffer solution, and from 101.6 to 111.1 ppm in the pH 9 phosphate buffer solution. No pattern of decline was noted in any set of samples. In all samples, inorganic chloride was <1.5 ppm. The pH of the buffer solutions remained stable throughout the study.

161-2 Aqueous Photolysis (MRID# 42900201)

This study provides very limited supplemental information. A new study is required. However, the study provides some information about the nature of the photolysis products of chloropicrin. Major problems were found in this study related to the material balance.

Chloropicrin, at 164 mg/L, photodegraded with a registrant-calculated half-life of 31.1 hours (1.29 days) in sterile aqueous solutions buffered at pH 7 at 25□C, irradiated with a xenon arc lamp (at about twice the intensity of natural sunlight in April in Hollister, California) on a 12 hour photoperiod. In contrast, the dark controls did not appear to hydrolyze substantially during the test period.

$$CCl_3NO_2 \xrightarrow[H_2O]{hv} 3Cl^- + NO_2^- + NO_3^- + CO_2 + H^+ \quad (HCO_3^- + CO_2^{2-})$$

Chloride increased to up to 0.00240 M (80%) after 108 hours. CO_2 increased to up to 0.000143 M (14.3%) after 108 hours. The bicarbonate ion increased to 0.000573 M after 108 hours. Other products were nitrate and nitrite, at maximum of 0.000347 M and 0.000143 M, at 108 hours, respectively. The chloride ion reached 0.00205 M after 108 hours.

161-3 Photodegradation on Soil (Waived)

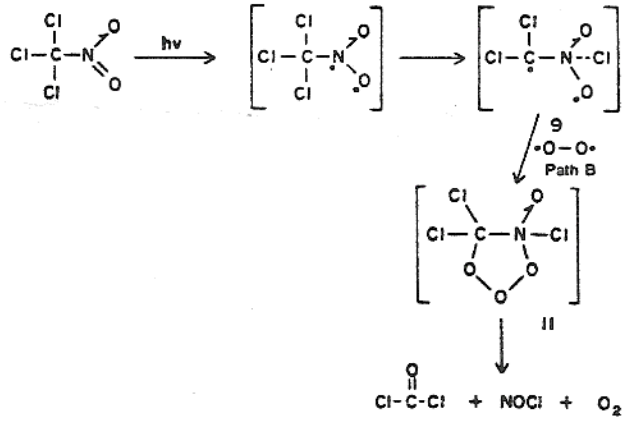
This study was waived because chloropicrin is used by soil injections, therefore, no substantial soil photolysis is expected.

161-4 Photolysis in Air (MRID# 05007865)

The photolytic half-life of chloropicrin vapor is about 20 days at 25-30□C. The photolysis rate decreased markedly after 20 days. The photodegradation appears to be dependent on the presence of oxygen. The initial photoproducts and the incorporation of $^{18}O_2$ suggest an intramolecular rearrangement involving the trioxazole N-oxide as an intermediate. In the dark control, the concentration of chloropicrin decreased slightly over 70 days.

Chloropicrin vapor is readily photodegraded to phosgene ($COCl_2$) and nitrosyl chloride (NOCl) under simulated sunlight. $COCl_2$ is not further degraded, but NOCl subsequently is photodegraded to nitrous oxide (NO) and chlorine (Cl_2). A portion of the NO is oxidized to nitrogen dioxide (NO_2) and dinitrogen tetraoxide (N_2O_4).

A degradation pathway was postulated by the registrant: In nitrogen atmosphere, chloropicrin was stable to irradiation, indicating that O_2 is required for photodecomposition, and suggesting that an intermediate, trioxazole N-oxide, was involved, that decomposes to $COCl_2$, NOCl, and O_2.



Postulated pathway for the photodegradation of chloropicrin.

162-1 Aerobic Soil Metabolism (MRID# 43613901)

This aerobic soil metabolism study is scientifically valid and provides useful information on the aerobic soil metabolism of chloropicrin. The study is acceptable as it followed the previously approved protocol for the data requirement. No new study is required.The registrant is required to address the following problems found in the study:

- Maintenance of aerobic conditions and moisture at the water holding capacity (WHC) throughout the experiment;
- Effects of chloropicrin on soil viability;
- Location of the PUF trap in relation to the KOH trap; and
- The target thickness, in inches, of the soil to be treated in th field and its vertical location in the soil profile.

[^{14}C]chloropicrin, at nominal application rates of 310-329 ppm, or equivalent field rates of nearly 550-600 lb a.i/acre, degraded in the laboratory with calculated half-life of 8 to 11 days in Baywood sandy loam soil adjusted to 78% of 0.33 bar moisture and incubated in the dark at 25±1^{o}C for up to 21 and 24 days.

The study was performed using three samples sets which were not treated at the same rate or incubated simultaneously. The study indicates that biotic transformation into CO_2 is the most important process that had governed the fate of chloropicrin under the stated laboratory conditions. Initially, parent escaped biodegradation by volatilization but later was subject to biodegradation and to binding, into the soil, in a non-extractable form.

Evolved $^{14}CO_2$ increased to 72.2% at 24 days posttreatment. Chloronitromethane, nitromethane, and bicarbonate were the only three minor degradates identified (a total of <6% of the applied radioactivity). Degradates were formed by substitution of Cl by H and were mainly detected in association with the soil in extractable and later in nonextractable forms.

This aerobic soil study was conducted without supplying the system with continuous flow to remove volatile materials. This type of system do not closely mimic field condition where volatilized materials are relatively free to escape.

Reexamination of the study results reveals that volatilization, in the soil environment, will be the major dissipation route of chloropicrin. Due to the fact that volatilization is significant and occurs rapidly, the importance of other competing processes such as leaching, biodegradation, and adsorption to the soil particles will certainly depend on expected field volatility. This is because volatility determines the amount of chloropicrin left for other processes and its residence time in the soil system.

162-3 Anaerobic Aquatic Metabolism (MRID# 43759301, supplemental)

This study provides useful supplemental information about the anaerobic aquatic metabolism of chloropicrin. The study does not meet Subdivision N Guidelines for the fulfillment of EPA data requirements for the following reasons:

- The test water was not representative of that found at an intended use site (purified deionized water was utilized to flood the soil samples).
- The analytical methods were inadequate for the characterization of residues in water samples removed at later sampling intervals. The HPLC column recoveries for the water phase samples were 103-104% at 0-1.5 hours posttreatment, decreased to 83.6% by 5 days posttreatment, and were 24.1% at 54 days posttreatment. The study authors did not provide an explanation for this decrease.

Radiolabeled [^{14}C]chloropicrin, at a nominal application rate of 313 ± 14.4 µg/g, degraded with a calculated half-life of 1.3 hours (r^2 = 1.0; 0- to 4-hour data only) in anaerobic flooded sandy loam soil that was incubated in darkness at 25 ± 1 □C for up to 54 days.

All data are reported as percentages of the nominal application. Degradate data are reported in parent equivalents. The parent was initially present in the total soil/water system at 96.3% of the applied radioactivity, decreased to 45.5% by 1.5 hours and 11.2% by 4 hours, was 1.7-2.2% at 1-2 days, was not detected from 5 to 12 days, and was last detected at 0.1% (one of two replicates) at 26 days posttreatment. The parent was mostly associated with the water phase.

The major degradate nitromethane was a maximum of 53.4% at 1 day, and was last detected at 16.9% (one of two replicates) at 26 days posttreatment.

The major degradate chloronitromethane increased to 51.5% by 4 hours, and was last detected at 0.1% (one of two replicates) at 54 days posttreatment.

Nonextractable [^{14}C]residues increased to a maximum of 32.0% at 54 days posttreatment; [^{14}C]residues associated with the fulvic and humic acid fractions were 24.4% and 1.3% of the applied, respectively, at 54 days posttreatment.

[^{14}C]Volatiles in the KOH traps reached 45.7% at 54 days posttreatment. Based on $BaCl_2$ precipitation of KOH traps, evolved $^{14}CO_2$ accounted for 4.1% at 54 days posttreatment.

[^{14}C]Organic volatiles were a maximum of 8.8% of the applied radioactivity at 1.5 hours, were 2.5-4.9% at 1-5 days, and were 0.6% at 54 days posttreatment. Based on HPLC analysis of the foam plug extract, the parent accounted for 8.1% of the applied radioactivity at 1.5 hours and was 1.1-1.8% at 1-2 days posttreatment. Radioactivity in the headspace was 10.9% of the applied radioactivity at 1.5 hours and was 0.1-0.7% at 1-54 days posttreatment; the parent accounted for 10.7% of the applied at 1.5 hours posttreatment.

163-1 Mobility - Column Leaching (MRID# 44191301)

This study is considered acceptable and it meets Subdivision §N Guidelines for the fulfillment of the mobility data requirement (column leaching) of chloropicrin. However, data were variable for the silty clay loam soil and the loamy sand soil, precluding definitive mobility determinations for the compound in those soils.

The column leaching of [^{14}C]chloropicrin, at a nominal rate equivalent to 345 lb/A or 362 lb/A was studied in sandy loam, loamy sand, silt loam, and silty clay loam soil columns which were leached with $CaCl_2$ over a period of 17-138 hours, 1-1.5 hours, 126-132 hours, and 101-116 hours, respectively. Based on the results of this study, it was observed that chloropicrin is very mobile in all four soils tested.

In the Baywood sandy loam soil, most of the [^{14}C]residues retained in the soil column following leaching were detected in the 30- to 36-cm (4.6%), 36- to 42-cm (5.7%), and 42- to 48-cm (5.7%) depths. The parent was 4.0% of the applied radioactivity in the 12- to 24-cm depth (12- to 18-cm and 18- to 24-cm depths combined), was 6.9% in the 24- to 36-cm depth (24- to 30-cm and 30- to 36-cm depths combined), and was 11.2% in the 36- to 48-cm depth (36- to 42-cm and 42- to 48-cm depths combined). The minor degradates dichloronitromethane, and nitromethane were detected once each. Nonextractable [^{14}C]residues were 1.0% of the applied radioactivity in the 12- to 18-cm depth, and were 0.4-0.5% in each of the 18- to 24-cm, 30- to 36-cm, 36- to 42-cm, 24- to 30-cm, and 42- to 48-cm depths. Total [^{14}C]residues in the leachate solution were 30.8% of the applied radioactivity. The parent was 17.2% of that radioactivity; the minor degradates dichloromethylhydroxylamine, dichloronitromethane, and nitromethane were ≤7.3% of the applied radioactivity. [^{14}C]Organic volatiles (bottom of the column) were 32.8% of the applied radioactivity; the parent accounted for 32.4% of the applied.

In the Baywood loamy sand soil, most of the [^{14}C]residues retained in the soil column following leaching were detected in the 12- to 18-cm (22.6%) depth. The parent was 36.6% (two of three columns) of the applied radioactivity in the 12- to 24-cm depth (12- to 18-cm and 18- to 24-cm depths combined) and was 8.6% (two of three columns) in the 24- to 48-cm depth (24- to 30-cm, 30- to 36-cm, 36- to 42-cm, and 42- to 48-cm depths combined). Degradates were not detected. Nonextractable [^{14}C]residues were 0.1% of the applied radioactivity in each of the 18- to 24-cm, 24- to 30-cm, 30- to 36-cm, 36- to 42-cm, and 42- to 48-cm depths. Total [^{14}C]residues in the leachate solution were 43.7% of the applied radioactivity. The parent was 42.7% of the applied radioactivity. The minor degradates dichloronitromethane and dichloromethyl hydroxylamine were each ≤0.77% of the applied radioactivity. [^{14}C]Organic volatiles (bottom of the column) were 12.2% of the applied radioactivity; the parent accounted for 12.2% of the applied.

In the Congaree silt loam soil, most of the [^{14}C]residues retained in the soil column following leaching were detected in the 36- to 42-cm (6.6%) and 42- to 48-cm (6.9%) depths. The parent was 0.1% of the applied radioactivity in each of the 12- to 30-cm (combined), 30- to 42-cm (combined), and 42- to 48-cm depths. The minor degradates dichloromethylhydroxylamine, dichloronitromethane, and nitromethane were detected at ≤0.1% of the applied radioactivity. Nonextractable [^{14}C]residues were 0.4% of the applied radioactivity in the 6- to 12-cm depth,

were 2.5-4.5% in each of the 12- to 18-cm, 18- to 24-cm, and 24- to 30-cm depth, and were 5.0-5.7% in each of the 30- to 36-cm, 36- to 42-cm, and 42- to 48-cm depths; [^{14}C]residues associated with the humic acid, fulvic acid, and humin fractions of a selected soil column were 0.19-0.38%, 0.94-2.8%, and 1.9-4.1% of the applied, respectively, in each of the 12- to 18-cm, 18- to 24-cm, 24- to 30-cm, 30- to 36-cm, 36- to 42-cm, and 42- to 48-cm depths. Total [^{14}C]residues in the leachate solution were 31.6% of the applied radioactivity. The parent was 1.1% of the applied radioactivity. The major degradate dichloromethylhydroxylamine was 16.4% of the applied radioactivity. The major degradate dichloronitromethane was 10.9% of the applied radioactivity. The minor degradate nitromethane was 2.5% of the applied radioactivity. [^{14}C]Organic volatiles (bottom of column) were 17.8% of the applied radioactivity; the parent and dichloronitromethane accounted for 13.8% and 3.3% of the applied, respectively.

In the Lowell silty clay loam soil, most of the [^{14}C]residues retained in the soil column following leaching were detected in the 12- to 18-cm (24.3%) depth. Characterization data were variable between the two soil columns. In Column 1, the parent was 0.1% of the applied radioactivity in each of the 12- to 30-cm, 30- to 42-cm, and 42- to 48-cm depths. In Column 2, the parent was 49.3% of the applied radioactivity in the 12- to 24-cm depth, was 1.3% in the 24- to 36-cm depth, and was not detected in the 36- to 48-cm depth. The minor degradates dichloronitromethane, and dichloromethylhydroxylamine were ≤1.5% of the applied radioactivity. Nonextractable [^{14}C]residues were ≤2.2% of the applied radioactivity in each of the soil depth from 6- to 42-cm; [^{14}C]residues associated with the humic acid, fulvic acid, and humin fractions of combined soil columns (12 to 48-cm depth) were 0.5%, 6.3%, and 6.0% of the applied, respectively. Total [^{14}C]residues in the leachate solution were 20.5% of the applied radioactivity. The parent compound was present at 1.5% (one of two column leachates) of the applied radioactivity. The major degradate dichloronitromethane was 12.0% of the applied radioactivity. The minor degradates dichloromethylhydroxylamine, and nitromethane were ≤5.5% of the applied radioactivity. [^{14}C]Organic volatiles (bottom of column) were 19.4% of the applied radioactivity; the parent accounted for 14.5% (one of two columns) of the applied. The major degradate dichloronitromethane was detected at 10.3% of the applied radioactivity. The minor degradate nitromethane was 1.5% of the applied radioactivity. The minor degradate dichloromethyl-hydroxylamine was 0.6% of the applied radioactivity.

163-2 Laboratory Volatility (MRID# 43798601)

This study is acceptable as it meets Subdivision N Guidelines for the fulfillment of EPA data requirements on laboratory volatility. This laboratory volatility study is scientifically valid. It provides useful information on the volatility of chloropicrin in a sandy loam soil. However, it appears that the flow exchange rate is high compared to actual use conditions.

The registrant is required to address the following:

- Time zero analysis of treated soil was not conducted;
- Was the trapping efficiencies of charcoal, methanol, and KOH traps determined? if so give the results.

- Need to relate the 100 mL/min flow rate or corresponding air changes/hr to total exchanges during actual practice under greenhouse, and field conditions (specified wind speeds).
- Limits of detection were reported but limits of quantitation were not;
- What is the vapor pressure at 25 ^{o}C? Other references give 23.8 mm Hg; Is this accurate?

Although [^{14}C]chloropicrin was applied through sub-surface injection, it volatilized within few to nearly 30 hours from non-tarped and tarped soil surfaces, respectively. By the end of the 8-day laboratory experiment, 80-87% of the applied parent volatilized from the soil surface as parent, 5-8% volatilized as CO_2, 5-7% bound to the soil, and <1% degraded into chloronitromethane. The results indicate that volatilization as parent, is expected to be the most important route of dissipation for chloropicrin in the soil environment. Data on non-tarped and tarped covered soil surfaces indicate that covering the soil surface with plastic tarp caused a change in the pattern and rates of volatilization during the first 60 hours of the experiment.

[^{14}C]chloropicrin, at a nominal application rate of 300 ppm, volatilized from sandy loam soil (uncovered and tarp-covered) adjusted to 60% of 0.33 bar soil moisture content and incubated in darkness at 25.0 ± 1 □C for up to 8 days with an air flow (>90% relative humidity) rate of approximately 100 mL/min.

In the uncovered (no tarp) soil, the maximum volatility of the parent was 342 µg/cm^2/hr and the maximum air concentration of the parent was 1.0 × 10^4 µg × 10^3/m^3 (2-6 hour interval). Total [^{14}C]volatiles accounted for 92.6% of the applied radioactivity at 8 days posttreatment. Organic [^{14}C]volatiles detected in the methanol, water vapor, and charcoal traps were 86.0%, 1.5%, and 0.08% of the applied radioactivity, respectively, at 8 days posttreatment; evolved $^{14}CO_2$ was 5.1% of the applied. The parent was initially (2 hours) present in the methanol trap at 0.8% of the applied radioactivity, increased to 16.3% by 6 hours and 65.4% by 24 hours, and was 81.5-85.5% at 46-116 hours posttreatment. The degradate dichloronitromethane was detected in the methanol trap at 0.4% of the applied radioactivity. In the soil, extractable and nonextractable [^{14}C]residues were 0.4% and 4.3% of the applied radioactivity, respectively, at 8 days posttreatment.

In tarp covered soil, the pesticide stayed within the soil system for relatively longer period of time than in non-tarped soil. This resulted in a slightly higher pesticide bio-degradation and binding to the tarped compared to non-tarped soil as inferred from the observed higher concentrations of CO_2 and soil bound residue. In the tarp-covered soil, the maximum volatility of the parent was 205 µg/cm^2/hr and the maximum air concentration of the parent was 5918 µg × 10^3/m^3 (23-25 hour interval; interval in which the tarp was punctured). Total [^{14}C]volatiles accounted for 89.3% of the applied radioactivity at 8 days posttreatment. Organic [^{14}C]volatiles detected in the methanol, water vapor, and charcoal traps were 79.9%, 1.2%, and 0.09% of the applied radioactivity, respectively, at 8 days posttreatment; evolved $^{14}CO_2$ was 8.2% of the applied. The parent was initially (4 hours) present in the methanol trap at 1.9% of the applied radioactivity, increased to 38.7% by 23 hours and 67.2% by 47 hours, and was 79.1% at 144 hours posttreatment. The degradate dichloronitromethane was detected in the methanol trap at 0.7% of

the applied radioactivity. In the soil, extractable and nonextractable [^{14}C]residues were 1.1% and 6.1% of the applied radioactivity, respectively, at 8 days posttreatment.

164-1 Terrestrial Field Dissipation (MRID# 43085101, supplemental)

This study provides limited supplemental information about the terrestrial field dissipation of chloropicrin. Several problems were found in the study:

- samples were taken only of the soil air and analyzed only for chloropicrin (and methyl bromide), no soil samples were taken;
- the test soils were not completely characterized;
- the site description was incomplete and not adequately characterized;
- the field maintenance practices used before and after application were not provided.

Chloropicrin dissipated with half-lives of 11.6, 16.4, and 33.4 hours from the soil air at the 3-, 6-, and 12-inch depths, respectively, following treatment with 665 lb a.i./A chloropicrin (TRI-CLOR: 99% purity) of a tarped clay loam soil in California in July, 1987. The chloropicrin was applied by chisel injection at a depth of 6-8 inches, the soil surface was covered with a polyethylene tarp for 48 hours, and sampling was initiated after removal of the tarp. Chloropicrin was found at maximum concentration of 755-781 ppm in the soil air from the upper 12 inches at 51 hours posttreatment (3 hours after removal of the tarp). Concentrations at the 24-, 36-, and 48-inch depths were never exceeded 30, 8.6, and 5.8 ppm, respectively, and declined to below background levels by the termination of the study (291 hours posttreatment). Background levels of chloropicrin (as determined by analysis of soil air from the untreated check plot located 15 feet away from the treated plot) ranged from 0.2 to 8.5 ppm (average 2.9 ppm).

Chloropicrin dissipated with half-lives of 18.0, 20.3, and 28.7 hours from the soil air at the 3-, 6-, and 12-inch depths, respectively, following treatment with 792 lb a.i./A chloropicrin (TRI-CLOR: 99% purity) of a tarped sand soil in California in August, 1987. The chloropicrin was applied by chisel injection at a depth of 6-8 inches, the soil surface was covered with a polyethylene tarp for 48 hours, and sampling was initiated after removal of the tarp. Chloropicrin was found at maximum concentrations of 554.0, 930.0, and 1185.0 ppm in the 3-, 6-, and 12-inch soil depths, respectively, at 51 hours posttreatment (3 hours after removal of the tarp). Concentrations at the 24-, 36-, and 48-inch depths increased to a maxima of 593.0, 230.5, and 75.2 ppm, respectively; times of maximum concentration were 12, 12, and 48 hours, respectively, after removal of the tarp. By the termination of the study (240 hours posttreatment), concentrations at 24-, 36-, and 48-inch depths had decreased to 31.8, 37.1, and 16.8 ppm, respectively. Background levels of chloropicrin (as determined by analysis of soil air from the untreated check plot located 15 feet away from the treated plot) ranged from 0.3 to 8.5 ppm (average 1.9 ppm).

Appendix B. Aquatic Exposure PRZM/EXAMS Modeling

This appendix documents the output from PRZM / EXAMS simulations for each of six location/crop scenarios: California / Onion and Tomato, Florida / Strawberry and Tomato, and North Carolina / Tobacco and sweet potato. The settings for each model run are presented first, followed by the raw data sorted by year and sorted in descending order by EEC. Values represent the estimated environmental concentrations (EECs) in units of micrograms per liter (μg/L) or parts per billion (ppb). The 1-in-10 year summary statistics for each run are presented at the very end of the sorted results in the row assigned a probability level of 0.10. This summary statistic was generated from a linear interpretation of the raw data plotted using Weibull plotting positions. This approach is further described at the end of the appendix B-6.

B.1.1 Florida Strawberry

stored as FLStrawb.out
Chemical: Chloropicrin
PRZM environment: FlstrawberryC.txt, Modified Monday, 30 June 2003 at 08:19:10
EXAMS environment: pond298.exv, Modified Thuday, 29 August 2002 at 16:33:30
Metfile: w12842.dvf, Modified Wedday, 3 July 2002 at 09:04:28

Water segment concentrations (ppb)

Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
1961	4.62	3.11	1.38	0.57	0.39	0.10
1962	84.41	57.97	21.99	8.16	5.45	1.34
1963	33.19	22.05	8.17	3.42	2.30	0.57
1964	3.16	2.18	1.15	0.53	0.36	0.09
1965	104.00	69.55	26.30	9.81	6.55	1.62
1966	5.05	3.58	2.12	0.91	0.61	0.15
1967	6.91	4.70	2.87	1.18	0.79	0.20
1968	8.70	5.98	2.72	1.19	0.81	0.20
1969	12.37	8.54	3.85	1.59	1.09	0.27
1970	9.06	6.21	2.81	1.18	0.80	0.20
1971	6.26	4.40	2.64	1.05	0.71	0.17
1972	8.03	6.09	2.53	1.24	0.83	0.20
1973	12.09	8.28	4.75	2.08	1.40	0.35
1974	6.28	4.33	2.06	0.84	0.56	0.14
1975	14.37	9.83	4.59	1.98	1.33	0.33
1976	9.72	6.82	3.89	1.91	1.29	0.32
1977	60.94	44.11	17.73	6.73	4.49	1.11
1978	9.81	6.99	4.60	1.86	1.24	0.31
1979	16.43	13.15	6.33	2.49	1.67	0.41
1980	8.42	6.11	2.81	1.14	0.77	0.19
1981	24.23	18.26	8.82	3.67	2.46	0.61
1982	49.07	36.61	16.95	6.34	4.23	1.04
1983	8.85	6.38	3.01	1.46	0.98	0.24
1984	3.25	2.25	1.53	0.67	0.45	0.11
1985	5.84	4.05	2.61	1.41	0.95	0.23
1986	12.51	9.87	4.56	1.74	1.17	0.29
1987	5.41	3.94	1.83	0.75	0.50	0.12
1988	9.87	6.79	3.38	1.69	1.14	0.28
1989	10.91	7.70	3.38	1.55	1.05	0.26
1990	3.08	2.24	1.32	0.50	0.33	0.08

Sorted results

Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.03	104.00	69.55	26.30	9.81	6.55	1.62
0.06	84.41	57.97	21.99	8.16	5.45	1.34
0.10	60.94	44.11	17.73	6.73	4.49	1.11
0.13	49.07	36.61	16.95	6.34	4.23	1.04
0.16	33.19	22.05	8.82	3.67	2.46	0.61

0.19	24.23	18.26	8.17	3.42	2.30	0.57
0.23	16.43	13.15	6.33	2.49	1.67	0.41
0.26	14.37	9.87	4.75	2.08	1.40	0.35
0.29	12.51	9.83	4.60	1.98	1.33	0.33
0.32	12.37	8.54	4.59	1.91	1.29	0.32
0.35	12.09	8.28	4.56	1.86	1.24	0.31
0.39	10.91	7.70	3.89	1.74	1.17	0.29
0.42	9.87	6.99	3.85	1.69	1.14	0.28
0.45	9.81	6.82	3.38	1.59	1.09	0.27
0.48	9.72	6.79	3.38	1.55	1.05	0.26
0.52	9.06	6.38	3.01	1.46	0.98	0.24
0.55	8.85	6.21	2.87	1.41	0.95	0.23
0.58	8.70	6.11	2.81	1.24	0.83	0.20
0.61	8.42	6.09	2.81	1.19	0.81	0.20
0.65	8.03	5.98	2.72	1.18	0.80	0.20
0.68	6.91	4.70	2.64	1.18	0.79	0.20
0.71	6.28	4.40	2.61	1.14	0.77	0.19
0.74	6.26	4.33	2.53	1.05	0.71	0.17
0.77	5.84	4.05	2.12	0.91	0.61	0.15
0.81	5.41	3.94	2.06	0.84	0.56	0.14
0.84	5.05	3.58	1.83	0.75	0.50	0.12
0.87	4.62	3.11	1.53	0.67	0.45	0.11
0.90	3.25	2.25	1.38	0.57	0.39	0.10
0.94	3.16	2.24	1.32	0.53	0.36	0.09
0.97	3.08	2.18	1.15	0.50	0.33	0.08
0.10	**59.75**	**43.36**	**17.65**	**6.69**	**4.47**	**1.10**
				Average of yearly averages:		0.38

Inputs generated by pe4.pl - 8-August-2003
Data used for this run:
Output File: FLStrawb
Metfile: w12842.dvf
PRZM scenario: FLstrawberryC.txt
EXAMS environment file: pond298.exv
Chemical Name: Chloropicrin

Description	Variable Name	Value	Units	Comments
Molecular weight	mwt	164.4	g/mol	
Henry's Law Const.	henry	0.00205	atm-m^3/mol	
Vapor Pressure	vapr	23.8	torr	
Solubility	sol	1621	mg/L	

Kd	Kd		mg/L	
Koc	Koc	36.05	mg/L	
Photolysis half-life	kdp	1.3	days	Half-life
Aerobic Aquatic Metabolism	kbacw	31.42	days	Halfife
Anaerobic Aquatic Metabolism	kbacs	0.05	days	Halfife
Aerobic Soil Metabolism	asm	15.71	days	Halfife
Hydrolysis:	pH 7	0	days	Half-life
Method:	CAM	8	integer	See PRZM manual
Incorporation Depth:	DEPI	25	cm	
Application Rate:	TAPP	392	kg/ha	
Application Efficiency:	APPEFF	1	fraction	
Spray Drift	DRFT	0	fraction of application rate applied to pond	
Application Date	Date	15-9	dd/mm or dd/mmm or dd-mm or dd-mmm	
Record 17:	FILTRA IPSCND UPTKF	1		
Record 18:	PLVKRT PLDKRT FEXTRC	0		
Flag for Index Res. Run	IR	Pond		
Flag for runoff calc.	RUNOFF	none	none, monthly or total(average of entire run)	

B.1.2 Florida Tomato

stored as FLTomato.out
Chemical: Chloropicrin
PRZM environment: FltomatoC.txt, Mmodified Satday, 12 October 2002 at 16:44:04
EXAMS environment: pond298.exv, Mmodified Thuday, 29 August 2002 at 16:33:30
Metfile: w12844.dvf, Modified Wedday, 3 July 2002 at 09:04:30

Water segment concentrations (ppb)

Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
1961	1.97	1.31	0.69	0.45	0.30	0.07
1962	106.00	79.75	29.59	10.54	7.03	1.73
1963	77.19	53.35	30.82	12.70	8.47	2.09
1964	56.35	38.79	19.41	7.97	5.33	1.31
1965	20.89	15.09	6.21	3.20	2.15	0.53
1966	24.46	17.68	7.92	3.41	2.27	0.56
1967	69.80	48.03	20.98	8.44	5.63	1.39
1968	55.26	44.23	24.24	9.56	6.37	1.57
1969	55.05	37.46	18.79	7.41	4.95	1.22
1970	31.83	21.15	9.60	3.46	2.31	0.57
1971	4.84	3.30	1.22	0.73	0.49	0.12
1972	1.49	1.03	0.36	0.13	0.09	0.02
1973	10.10	6.95	3.58	1.92	1.28	0.32
1974	21.65	12.56	6.02	2.28	1.53	0.38
1975	134.00	91.32	35.73	12.86	8.58	2.11
1976	4.26	2.83	1.16	0.69	0.47	0.11
1977	29.54	20.72	7.30	2.61	1.76	0.43
1978	12.72	8.86	3.67	1.58	1.06	0.26
1979	30.37	22.90	10.76	4.22	2.82	0.69
1980	13.06	8.86	2.94	1.29	0.87	0.21
1981	57.10	43.42	14.60	5.39	3.61	0.89
1982	20.74	14.47	6.84	2.64	1.76	0.43
1983	108.00	72.53	27.05	10.10	6.75	1.66
1984	64.45	46.78	21.74	7.87	5.29	1.30
1985	78.82	55.70	24.52	8.96	5.98	1.47
1986	4.07	2.68	0.84	0.55	0.38	0.10
1987	71.64	48.12	20.39	7.73	5.16	1.27
1988	4.06	2.68	0.85	0.32	0.21	0.05
1989	42.45	27.53	9.17	3.63	2.42	0.60
1990	198.00	132.00	46.46	16.59	11.06	2.73

Sorted results

Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.03	198.00	132.00	46.46	16.59	11.06	2.73
0.06	134.00	91.32	35.73	12.86	8.58	2.11
0.10	108.00	79.75	30.82	12.70	8.47	2.09
0.13	106.00	72.53	29.59	10.54	7.03	1.73
0.16	78.82	55.70	27.05	10.10	6.75	1.66

0.19	77.19	53.35	24.52	9.56	6.37	1.57
0.23	71.64	48.12	24.24	8.96	5.98	1.47
0.26	69.80	48.03	21.74	8.44	5.63	1.39
0.29	64.45	46.78	20.98	7.97	5.33	1.31
0.32	57.10	44.23	20.39	7.87	5.29	1.30
0.35	56.35	43.42	19.41	7.73	5.16	1.27
0.39	55.26	38.79	18.79	7.41	4.95	1.22
0.42	55.05	37.46	14.60	5.39	3.61	0.89
0.45	42.45	27.53	10.76	4.22	2.82	0.69
0.48	31.83	22.90	9.60	3.63	2.42	0.60
0.52	30.37	21.15	9.17	3.46	2.31	0.57
0.55	29.54	20.72	7.92	3.41	2.27	0.56
0.58	24.46	17.68	7.30	3.20	2.15	0.53
0.61	21.65	15.09	6.84	2.64	1.76	0.43
0.65	20.89	14.47	6.21	2.61	1.76	0.43
0.68	20.74	12.56	6.02	2.28	1.53	0.38
0.71	13.06	8.86	3.67	1.92	1.28	0.32
0.74	12.72	8.86	3.58	1.58	1.06	0.26
0.77	10.10	6.95	2.94	1.29	0.87	0.21
0.81	4.84	3.30	1.22	0.73	0.49	0.12
0.84	4.26	2.83	1.16	0.69	0.47	0.11
0.87	4.07	2.68	0.85	0.55	0.38	0.10
0.90	4.06	2.68	0.84	0.45	0.30	0.07
0.94	1.97	1.31	0.69	0.32	0.21	0.05
0.97	1.49	1.03	0.36	0.13	0.09	0.02
0.10	**107.80**	**79.03**	**30.70**	**12.48**	**8.33**	**2.05**
					Average of yearly averages:	0.87

Inputs generated by pe4.pl - 8-August-2003

Data used for this run:
Output File: FLTomato
Metfile: w12844.dvf
PRZM scenario: FLtomatoC.txt
EXAMS environment file: pond298.exv
Chemical Name: Chloropicrin

Description	Variable Name	Value	Units	Comments
Molecular weight	mwt	164.4	g/mol	
Henry's Law Const.	henry	0.00205	atm-m^3/mol	
Vapor Pressure	vapr	23.8	torr	
Solubility	sol	1621	mg/L	
Kd	Kd		mg/L	

Koc	Koc		36.05	mg/L	
Photolysis half-life	kdp		1.3	days	Half-life
Aerobic Aquatic Metabolism	kbacw		31.42	days	Halfife
Anaerobic Aquatic Metabolism	kbacs		0.05	days	Halfife
Aerobic Soil Metabolism	asm		15.71	days	Halfife
Hydrolysis:	pH 7		0	days	Half-life
Method:	CAM		8	integer	See PRZM manual
Incorporation Depth:	DEPI		25	cm	
Application Rate:	TAPP		392	kg/ha	
Application Efficiency:	APPEFF		1	fraction	
Spray Drift	DRFT		0	fraction of application rate applied to pond	
Application Date	Date	15-9		dd/mm or dd/mmm or dd-mm or dd-mmm	
Record 17:	FILTRA				
	IPSCND		1		
	UPTKF				
Record 18:	PLVKRT				
	PLDKRT				
	FEXTRC		0		
Flag for Index Res. Run	IR	Pond			
Flag for runoff calc.	RUNOFF	none		none, monthly or total(average of entire run)	

B.2.1 California Tomato

stored as CATomato.out
Chemical: Chloropicrin
PRZM environment: CAtomatoC.txt Modified Wedday, 2 February 2005 at 12:45:10
EXAMS environment: pond298.exv, Modified Thuday, 29 August 2002 at 16:33:30
Metfile: w93193.dvf, Modified Wedday, 3 July 2002 at 09:04:24

Water segment concentrations (ppb)

Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
1961	0.28	0.23	0.15	0.06	0.04	0.01
1962	0.44	0.34	0.15	0.05	0.04	0.01
1963	1.77	1.43	0.77	0.40	0.28	0.07
1964	2.50	1.90	0.91	0.36	0.24	0.06
1965	0.11	0.09	0.05	0.02	0.02	0.01
1966	0.52	0.46	0.27	0.13	0.09	0.02
1967	0.24	0.19	0.10	0.04	0.03	0.01
1968	2.23	1.75	0.85	0.49	0.34	0.09
1969	0.17	0.15	0.08	0.03	0.02	0.01
1970	0.28	0.22	0.13	0.06	0.04	0.01
1971	0.12	0.10	0.04	0.02	0.01	0.00
1972	0.50	0.42	0.26	0.11	0.07	0.02
1973	1.73	1.35	0.60	0.25	0.18	0.04
1974	6.62	5.11	2.42	1.00	0.67	0.17
1975	1.31	1.03	0.52	0.21	0.14	0.04
1976	4.19	3.30	1.48	0.63	0.43	0.11
1977	0.72	0.58	0.25	0.09	0.06	0.02
1978	0.25	0.21	0.10	0.05	0.03	0.01
1979	0.35	0.29	0.14	0.06	0.04	0.01
1980	0.02	0.02	0.01	0.00	0.00	0.00
1981	0.20	0.15	0.08	0.04	0.02	0.01
1982	3.79	2.93	1.87	0.84	0.61	0.16
1983	0.80	0.58	0.25	0.17	0.13	0.03
1984	0.68	0.54	0.27	0.16	0.13	0.03
1985	0.66	0.52	0.26	0.18	0.12	0.03
1986	0.14	0.12	0.05	0.02	0.01	0.01
1987	0.21	0.16	0.08	0.05	0.03	0.01
1988	0.13	0.11	0.06	0.03	0.02	0.01
1989	0.14	0.10	0.04	0.01	0.01	0.00
1990	0.07	0.05	0.03	0.02	0.01	0.00

Sorted results

Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.03	6.62	5.11	2.42	1.00	0.67	0.17
0.06	4.19	3.30	1.87	0.84	0.61	0.16
0.10	3.79	2.93	1.48	0.63	0.43	0.11
0.13	2.50	1.90	0.91	0.49	0.34	0.09
0.16	2.23	1.75	0.85	0.40	0.28	0.07

0.19	1.77	1.43	0.77	0.36	0.24	0.06
0.23	1.73	1.35	0.60	0.25	0.18	0.04
0.26	1.31	1.03	0.52	0.21	0.14	0.04
0.29	0.80	0.58	0.27	0.18	0.13	0.03
0.32	0.72	0.58	0.27	0.17	0.13	0.03
0.35	0.68	0.54	0.26	0.16	0.12	0.03
0.39	0.66	0.52	0.26	0.13	0.09	0.02
0.42	0.52	0.46	0.25	0.11	0.07	0.02
0.45	0.50	0.42	0.25	0.09	0.06	0.02
0.48	0.44	0.34	0.15	0.06	0.04	0.01
0.52	0.35	0.29	0.15	0.06	0.04	0.01
0.55	0.28	0.23	0.14	0.06	0.04	0.01
0.58	0.28	0.22	0.13	0.05	0.04	0.01
0.61	0.25	0.21	0.10	0.05	0.03	0.01
0.65	0.24	0.19	0.10	0.05	0.03	0.01
0.68	0.21	0.16	0.08	0.04	0.03	0.01
0.71	0.20	0.15	0.08	0.04	0.02	0.01
0.74	0.17	0.15	0.08	0.03	0.02	0.01
0.77	0.14	0.12	0.06	0.03	0.02	0.01
0.81	0.14	0.11	0.05	0.02	0.02	0.01
0.84	0.13	0.10	0.05	0.02	0.01	0.01
0.87	0.12	0.10	0.04	0.02	0.01	0.00
0.90	0.11	0.09	0.04	0.02	0.01	0.00
0.94	0.07	0.05	0.03	0.01	0.01	0.00
0.97	0.02	0.02	0.01	0.00	0.00	0.00
0.10	**3.66**	**2.83**	**1.42**	**0.61**	**0.42**	**0.10**
					Average of yearly averages:	0.03

Inputs generated by pe4.pl - 8-August-2003

Data used for this run:
Output File: CATomato
Metfile: w93193.dvf
PRZM scenario: CAtomatoC.txt
EXAMS environment file: pond298.exv
Chemical Name: Chloropicrin

Description	Variable Name	Value	Units	Comments
Molecular weight	mwt	164.4	g/mol	
Henry's Law Const.	henry	0.00205	atm-m^3/mol	
Vapor Pressure	vapr	23.8	torr	
Solubility	sol	1621	mg/L	
Kd	Kd		mg/L	

Koc	Koc		36.05	mg/L	
Photolysis half-life	kdp		1.3	days	Half-life
Aerobic Aquatic Metabolism	kbacw		31.42	days	Halfife
Anaerobic Aquatic Metabolism	kbacs		0.05	days	Halfife
Aerobic Soil Metabolism	asm		15.71	days	Halfife
Hydrolysis:	pH 7		0	days	Half-life
Method:	CAM		8	integer	See PRZM manual
Incorporation Depth:	DEPI		25	cm	
Application Rate:	TAPP		392	kg/ha	
Application Efficiency:	APPEFF		1	fraction	
Spray Drift	DRFT		0	fraction of application rate applied to pond	
Application Date	Date	15-9		dd/mm or dd/mmm or dd-mm or dd-mmm	
Record 17:	FILTRA IPSCND UPTKF		1		
Record 18:	PLVKRT PLDKRT FEXTRC		0		
Flag for Index Res. Run	IR	Pond			
Flag for runoff calc.	RUNOFF	none		none, monthly or total(average of entire run)	

B.2.2 California Onion

stored as CAOnion.out
Chemical: Chloropicrin
PRZM environment: CAonionC.txt Modified Monday, 23 December 2002 at 06:48:48
EXAMS environment: pond298.exv, Modified Thuday, 29 August 2002 at 16:33:30
Metfile: w23155.dvf, Modified Wedday, 3 July 2002 at 09:04:20

Water segment concentrations (ppb)

Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
1961	0.02	0.02	0.01	0.00	0.00	0.00
1962	0.00	0.00	0.00	0.00	0.00	0.00
1963	15.87	11.74	4.63	1.73	1.15	0.28
1964	0.19	0.14	0.06	0.02	0.02	0.00
1965	0.06	0.05	0.02	0.01	0.01	0.00
1966	0.06	0.05	0.03	0.02	0.01	0.00
1967	0.10	0.09	0.05	0.02	0.02	0.00
1968	0.49	0.39	0.19	0.08	0.06	0.01
1969	0.04	0.03	0.01	0.00	0.00	0.00
1970	0.06	0.04	0.02	0.01	0.01	0.00
1971	0.01	0.00	0.00	0.00	0.00	0.00
1972	0.29	0.23	0.10	0.06	0.04	0.01
1973	0.01	0.01	0.01	0.00	0.00	0.00
1974	5.68	4.26	1.70	0.65	0.44	0.11
1975	0.01	0.00	0.00	0.00	0.00	0.00
1976	0.50	0.35	0.13	0.05	0.03	0.01
1977	0.03	0.02	0.00	0.00	0.00	0.00
1978	0.02	0.01	0.01	0.00	0.00	0.00
1979	0.00	0.00	0.00	0.00	0.00	0.00
1980	0.00	0.00	0.00	0.00	0.00	0.00
1981	1.94	1.48	0.61	0.23	0.15	0.04
1982	2.16	1.56	0.60	0.24	0.17	0.04
1983	0.09	0.07	0.03	0.02	0.01	0.00
1984	0.06	0.04	0.02	0.01	0.01	0.00
1985	0.35	0.28	0.13	0.06	0.04	0.01
1986	0.03	0.02	0.01	0.01	0.00	0.00
1987	1.44	1.15	0.53	0.20	0.14	0.03
1988	0.00	0.00	0.00	0.00	0.00	0.00
1989	1.09	0.68	0.20	0.07	0.05	0.01
1990	0.00	0.00	0.00	0.00	0.00	0.00

Sorted results

Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.03	15.87	11.74	4.63	1.73	1.15	0.28
0.06	5.68	4.26	1.70	0.65	0.44	0.11
0.10	2.16	1.56	0.61	0.24	0.17	0.04
0.13	1.94	1.48	0.60	0.23	0.15	0.04
0.16	1.44	1.15	0.53	0.20	0.14	0.03
0.19	1.09	0.68	0.20	0.08	0.06	0.01

0.23	0.50	0.39	0.19	0.07	0.05	0.01
0.26	0.49	0.35	0.13	0.06	0.04	0.01
0.29	0.35	0.28	0.13	0.06	0.04	0.01
0.32	0.29	0.23	0.10	0.05	0.03	0.01
0.35	0.19	0.14	0.06	0.02	0.02	0.00
0.39	0.10	0.09	0.05	0.02	0.02	0.00
0.42	0.09	0.07	0.03	0.02	0.01	0.00
0.45	0.06	0.05	0.03	0.02	0.01	0.00
0.48	0.06	0.05	0.02	0.01	0.01	0.00
0.52	0.06	0.04	0.02	0.01	0.01	0.00
0.55	0.06	0.04	0.02	0.01	0.01	0.00
0.58	0.04	0.03	0.01	0.01	0.00	0.00
0.61	0.03	0.02	0.01	0.00	0.00	0.00
0.65	0.03	0.02	0.01	0.00	0.00	0.00
0.68	0.02	0.02	0.01	0.00	0.00	0.00
0.71	0.02	0.01	0.01	0.00	0.00	0.00
0.74	0.01	0.01	0.00	0.00	0.00	0.00
0.77	0.01	0.00	0.00	0.00	0.00	0.00
0.81	0.01	0.00	0.00	0.00	0.00	0.00
0.84	0.00	0.00	0.00	0.00	0.00	0.00
0.87	0.00	0.00	0.00	0.00	0.00	0.00
0.90	0.00	0.00	0.00	0.00	0.00	0.00
0.94	0.00	0.00	0.00	0.00	0.00	0.00
0.97	0.00	0.00	0.00	0.00	0.00	0.00
0.10	**2.14**	**1.55**	**0.61**	**0.24**	**0.17**	**0.04**

Average of yearly averages: 0.02

Inputs generated by pe4.pl - 8-August-2003

Data used for this run:
Output File: CAOnion
Metfile: w23155.dvf
PRZM scenario: CAonionC.txt
EXAMS environment file: pond298.exv
Chemical Name: Chloropicrin

Description	Variable Name	Value	Units	Comments
Molecular weight	mwt	164.4	g/mol	
Henry's Law Const.	henry	0.00205	atm-m^3/mol	
Vapor Pressure	vapr	23.8	torr	
Solubility	sol	1621	mg/L	
Kd	Kd		mg/L	
Koc	Koc	36.05	mg/L	
Photolysis	kdp	1.3	days	Half-life

half-life					
Aerobic Aquatic Metabolism	kbacw		31.42	days	Halfife
Anaerobic Aquatic Metabolism	kbacs		0.05	days	Halfife
Aerobic Soil Metabolism	asm		15.71	days	Halfife
Hydrolysis:	pH 7		0	days	Half-life
Method:	CAM		8	integer	See PRZM manual
Incorporation Depth:	DEPI		25	cm	
Application Rate:	TAPP		392	kg/ha	
Application Efficiency:	APPEFF		1	fraction	
Spray Drift	DRFT		0	fraction of application rate applied to pond	
Application Date	Date	15-9		dd/mm or dd/mmm or dd-mm or dd-mmm	
Record 17:	FILTRA				
	IPSCND		1		
	UPTKF				
Record 18:	PLVKRT				
	PLDKRT				
	FEXTRC		0		
Flag for Index Res. Run	IR	Pond			
Flag for runoff calc.	RUNOFF	none		none, monthly or total(average of entire run)	

B.3.1 North Carolina Tobacco

stored as NCTobac.out
Chemical: Chloropicrin
PRZM environment: NctobaccoC.txt, modified Satday, 12 October 2002 at 17:13:36
EXAMS environment: pond298.exv, modified Thuday, 29 August 2002 at 16:33:30
Metfile: w13722.dvf,modified Wedday, 3 July 2002 at 09:05:50

Water segment concentrations (ppb)

Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
1961	0.67	0.49	0.18	0.07	0.04	0.01
1962	0.03	0.02	0.01	0.01	0.00	0.00
1963	0.61	0.46	0.21	0.08	0.05	0.01
1964	0.02	0.01	0.00	0.00	0.00	0.00
1965	0.14	0.11	0.04	0.02	0.01	0.00
1966	0.91	0.67	0.26	0.11	0.07	0.02
1967	0.97	0.70	0.41	0.17	0.12	0.03
1968	0.08	0.06	0.02	0.01	0.01	0.00
1969	0.07	0.05	0.03	0.01	0.01	0.00
1970	0.29	0.21	0.08	0.03	0.02	0.00
1971	0.25	0.18	0.08	0.04	0.02	0.01
1972	0.55	0.40	0.22	0.08	0.06	0.01
1973	1.68	1.26	0.48	0.18	0.12	0.03
1974	0.29	0.22	0.12	0.05	0.04	0.01
1975	0.07	0.06	0.02	0.01	0.01	0.00
1976	0.19	0.14	0.06	0.02	0.02	0.00
1977	0.07	0.05	0.02	0.01	0.01	0.00
1978	2.70	2.01	0.85	0.31	0.21	0.05
1979	0.08	0.06	0.04	0.03	0.02	0.00
1980	0.44	0.33	0.13	0.05	0.03	0.01
1981	0.19	0.14	0.06	0.02	0.01	0.00
1982	0.80	0.60	0.24	0.10	0.07	0.02
1983	0.05	0.04	0.02	0.01	0.01	0.00
1984	0.77	0.64	0.27	0.11	0.08	0.02
1985	1.26	0.93	0.36	0.14	0.09	0.02
1986	0.09	0.07	0.03	0.01	0.01	0.00
1987	0.01	0.01	0.00	0.00	0.00	0.00
1988	1.69	1.27	0.50	0.20	0.13	0.03
1989	1.67	1.22	0.47	0.17	0.12	0.03
1990	0.60	0.43	0.18	0.07	0.05	0.01

Sorted results

Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.03	2.70	2.01	0.85	0.31	0.21	0.05
0.06	1.69	1.27	0.50	0.20	0.13	0.03
0.10	1.68	1.26	0.48	0.18	0.12	0.03
0.13	1.67	1.22	0.47	0.17	0.12	0.03
0.16	1.26	0.93	0.41	0.17	0.12	0.03

0.19	0.97	0.70	0.36	0.14	0.09	0.02
0.23	0.91	0.67	0.27	0.11	0.08	0.02
0.26	0.80	0.64	0.26	0.11	0.07	0.02
0.29	0.77	0.60	0.24	0.10	0.07	0.02
0.32	0.67	0.49	0.22	0.08	0.06	0.01
0.35	0.61	0.46	0.21	0.08	0.05	0.01
0.39	0.60	0.43	0.18	0.07	0.05	0.01
0.42	0.55	0.40	0.18	0.07	0.04	0.01
0.45	0.44	0.33	0.13	0.05	0.04	0.01
0.48	0.29	0.22	0.12	0.05	0.03	0.01
0.52	0.29	0.21	0.08	0.04	0.02	0.01
0.55	0.25	0.18	0.08	0.03	0.02	0.00
0.58	0.19	0.14	0.06	0.03	0.02	0.00
0.61	0.19	0.14	0.06	0.02	0.02	0.00
0.65	0.14	0.11	0.04	0.02	0.01	0.00
0.68	0.09	0.07	0.04	0.02	0.01	0.00
0.71	0.08	0.06	0.03	0.01	0.01	0.00
0.74	0.08	0.06	0.03	0.01	0.01	0.00
0.77	0.07	0.06	0.02	0.01	0.01	0.00
0.81	0.07	0.05	0.02	0.01	0.01	0.00
0.84	0.07	0.05	0.02	0.01	0.01	0.00
0.87	0.05	0.04	0.02	0.01	0.01	0.00
0.90	0.03	0.02	0.01	0.01	0.00	0.00
0.94	0.02	0.01	0.00	0.00	0.00	0.00
0.97	0.01	0.01	0.00	0.00	0.00	0.00
0.10	**1.67**	**1.26**	**0.48**	**0.18**	**0.12**	**0.03**

Average of yearly averages: 0.01

Inputs generated by pe4.pl - 8-August-2003
Data used for this run:
Output File: NCTobac
Metfile: w13722.dvf
PRZM scenario: NCtobaccoC.txt
EXAMS environment file: pond298.exv
Chemical Name: Chloropicrin

Description	Variable Name	Value	Units	Comments
Molecular weight	mwt	164.4	g/mol	
Henry's Law Const.	henry	0.00205	atm-m^3/mol	
Vapor Pressure	vapr	23.8	torr	
Solubility	sol	1621	mg/L	
Kd	Kd		mg/L	

Koc	Koc		36.05	mg/L	
Photolysis half-life	kdp		1.3	days	Half-life
Aerobic Aquatic Metabolism	kbacw		31.42	days	Halfife
Anaerobic Aquatic Metabolism	kbacs		0.05	days	Halfife
Aerobic Soil Metabolism	asm		15.71	days	Halfife
Hydrolysis:	pH 7		0	days	Half-life
Method:	CAM		8	integer	See PRZM manual
Incorporation Depth:	DEPI		25	cm	
Application Rate:	TAPP		392	kg/ha	
Application Efficiency:	APPEFF		1	fraction	
Spray Drift	DRFT		0	fraction of application rate applied to pond	
Application Date	Date	15-4		dd/mm or dd/mmm or dd-mm or dd-mmm	
Record 17:	FILTRA				
	IPSCND		1		
	UPTKF				
Record 18:	PLVKRT				
	PLDKRT				
	FEXTRC		0		
Flag for Index Res. Run	IR	Pond			
Flag for runoff calc.	RUNOFF	none		none, monthly or total(average of entire run)	

B.3.2 North Carolina Sweet Potato

stored as NCsweet.out
Chemical: Chloropicrin
PRZM environment: NCSweetPotatoC.txt,modified Friday, 8 August 2003 at 09:25:48
EXAMS environment: pond298.exv, modified Thuday, 29 August 2002 at 16:33:30
Metfile: w13722.dvf, modified Wedday, 3 July 2002 at 09:05:50
Water segment concentrations (ppb)

Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
1961	1.21	0.96	0.37	0.14	0.09	0.02
1962	0.13	0.10	0.06	0.05	0.03	0.01
1963	0.97	0.73	0.36	0.14	0.10	0.02
1964	0.12	0.09	0.03	0.02	0.02	0.00
1965	0.32	0.23	0.12	0.06	0.05	0.01
1966	0.99	0.76	0.36	0.17	0.12	0.03
1967	0.51	0.36	0.15	0.11	0.09	0.02
1968	0.29	0.21	0.08	0.04	0.03	0.01
1969	0.21	0.16	0.09	0.04	0.04	0.01
1970	0.53	0.37	0.15	0.05	0.05	0.01
1971	0.33	0.26	0.13	0.06	0.05	0.01
1972	0.84	0.61	0.30	0.13	0.10	0.03
1973	1.77	1.34	0.51	0.21	0.15	0.04
1974	0.97	0.71	0.34	0.15	0.10	0.03
1975	0.29	0.23	0.11	0.06	0.05	0.01
1976	0.37	0.31	0.14	0.06	0.04	0.01
1977	0.27	0.20	0.09	0.04	0.03	0.01
1978	3.49	2.60	1.12	0.42	0.28	0.07
1979	0.31	0.23	0.16	0.08	0.05	0.01
1980	0.60	0.48	0.19	0.08	0.06	0.01
1981	0.33	0.25	0.12	0.06	0.04	0.01
1982	0.76	0.57	0.23	0.15	0.10	0.02
1983	0.20	0.15	0.08	0.03	0.02	0.01
1984	0.49	0.38	0.18	0.11	0.08	0.02
1985	1.46	1.08	0.44	0.18	0.14	0.04
1986	0.21	0.16	0.06	0.03	0.02	0.01
1987	0.04	0.03	0.01	0.01	0.00	0.00
1988	0.29	0.22	0.09	0.05	0.04	0.01
1989	1.40	1.08	0.46	0.18	0.12	0.03
1990	1.20	0.89	0.41	0.16	0.11	0.03

Sorted results

Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.03	3.49	2.60	1.12	0.42	0.28	0.07
0.06	1.77	1.34	0.51	0.21	0.15	0.04
0.10	1.46	1.08	0.46	0.18	0.14	0.04
0.13	1.40	1.08	0.44	0.18	0.12	0.03
0.16	1.21	0.96	0.41	0.17	0.12	0.03
0.19	1.20	0.89	0.37	0.16	0.11	0.03

0.23	0.99	0.76	0.36	0.15	0.10	0.03
0.26	0.97	0.73	0.36	0.15	0.10	0.03
0.29	0.97	0.71	0.34	0.14	0.10	0.02
0.32	0.84	0.61	0.30	0.14	0.10	0.02
0.35	0.76	0.57	0.23	0.13	0.09	0.02
0.39	0.60	0.48	0.19	0.11	0.09	0.02
0.42	0.53	0.38	0.18	0.11	0.08	0.02
0.45	0.51	0.37	0.16	0.08	0.06	0.01
0.48	0.49	0.36	0.15	0.08	0.05	0.01
0.52	0.37	0.31	0.15	0.06	0.05	0.01
0.55	0.33	0.26	0.14	0.06	0.05	0.01
0.58	0.33	0.25	0.13	0.06	0.05	0.01
0.61	0.32	0.23	0.12	0.06	0.05	0.01
0.65	0.31	0.23	0.12	0.06	0.04	0.01
0.68	0.29	0.23	0.11	0.05	0.04	0.01
0.71	0.29	0.22	0.09	0.05	0.04	0.01
0.74	0.29	0.21	0.09	0.05	0.04	0.01
0.77	0.27	0.20	0.09	0.04	0.03	0.01
0.81	0.21	0.16	0.08	0.04	0.03	0.01
0.84	0.21	0.16	0.08	0.04	0.03	0.01
0.87	0.20	0.15	0.06	0.03	0.02	0.01
0.90	0.13	0.10	0.06	0.03	0.02	0.01
0.94	0.12	0.09	0.03	0.02	0.02	0.00
0.97	0.04	0.03	0.01	0.01	0.00	0.00
0.10	**1.45**	**1.08**	**0.46**	**0.18**	**0.14**	**0.03**

Average of yearly averages: 0.02

Inputs generated by pe4.pl - 8-August-2003

Data used for this run:
Output File: NCsweet
Metfile: w13722.dvf
PRZM scenario: NCSweetPotatoC.txt
EXAMS environment file: pond298.exv
Chemical Name: Chloropicrin

Description	Variable Name	Value	Units	Comments
Molecular weight	mwt	164.4	g/mol	
Henry's Law Const.	henry	0.00205	atm-m^3/mol	
Vapor Pressure	vapr	23.8	torr	
Solubility	sol	1621	mg/L	
Kd	Kd		mg/L	
Koc	Koc	36.05	mg/L	

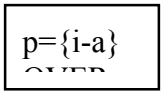
Photolysis half-life	kdp		1.3	days	Half-life
Aerobic Aquatic Metabolism	kbacw		31.42	days	Halfife
Anaerobic Aquatic Metabolism	kbacs		0.05	days	Halfife
Aerobic Soil Metabolism	asm		15.71	days	Halfife
Hydrolysis:	pH 7		0	days	Half-life
Method:	CAM		8	integer	See PRZM manual
Incorporation Depth:	DEPI		25	cm	
Application Rate:	TAPP		392	kg/ha	
Application Efficiency:	APPEFF		1	fraction	
Spray Drift	DRFT		0	fraction of application rate applied to pond	
Application Date	Date	15-4		dd/mm or dd/mmm or dd-mm or dd-mmm	
Record 17:	FILTRA				
	IPSCND		1		
	UPTKF				
Record 18:	PLVKRT				
	PLDKRT				
	FEXTRC		0		
Flag for Index Res. Run	IR	Pond			
Flag for runoff calc.	RUNOFF	none		none, monthly or total(average of entire run)	

B.4. Calculation of 1-in-10 year EEC using Weibull Probability Plots.

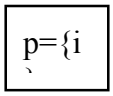
Output from the PRZM/EXAMS simulation is typically a series of estimated environmental concentrations (EEC) corresponding to multiple years of meteorological data. Each value is an estimate of the peak concentrations corresponding to a specific averaging time (e.g., 96 hours, 21 days, etc.). The 24-hour averaging time is sometimes referred to as the "Peak" concentration because the shortest time-step for a PRZM/EXAMS simulations is one day. Therefore, the column of EEC values reported in an output file for "Peak" refers to the maximum 24-hour EEC for each of the meteorological years.

For ecological risk assessment, it is important to match the averaging time to the duration of the toxicity study. However, of the multiple years of data, which EEC should be selected in the calculation of the RQ? The most conservative case would be to choose the maximum EEC for each averaging time. An alternative would be to calculate an upper end value that is less than the maximum. One statistic adopted by OPP for use in ecological risk assessment is the 1-in-10 year return value. This is the EEC that, on average, will be exceeded only once every 10 years. It is important to note that for any single 10-year period, the 1-in-10 year value may be exceeded more than once, or not at all. The key concept is that it represents the average probability of exceedance.

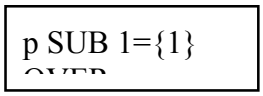
The 1-in-10 year statistic can be calculated using probability plotting methods. There are a number of different techniques, but a common practice in hydrology for plotting flow-duration and flood-frequency curves is to use the plotting position associated with the Weibull distribution (Helsel and Hirsch 1993). The general formula for probability plotting is given by:



where p is the probability level, n is the number of data points, and a is a coefficient that varies between 0 and 0.5. For the Weibull distribution, a is 0 so the plotting position is



For the PRZM/EXAMS simulations presented above, there are 30 years of meteorological data, so n = 30. To generate a Weibull probability plot to estimate the exceedance probabilities, the data should be sorted in descending order. That is, there is a lower probability of exceeding the maximum EEC than the second highest EEC. The plotting position associated with the maximum value is then calculated as follows:



The minimum and maximum probability values associated with the entire data set will approach [0, 1] as the sample size increases. Sometimes probability plots are used to estimate the values beyond the observed range. To calculate the 1-in-10 year statistic, we need the EEC associated with a probability value of 0.100. This value does not correspond directly with any of the modeled values, but it is between third highest value (p = 0.097) and fourth highest value (0.129). An interpolation procedure is needed to estimate the EEC associated with p = 0.100. A linear interpolation is commonly performed, although two methods are available. One method involves fitting a line to the entire set of data plotted on a Weibull probability plot. The second method involves a linear interpolation only between the two values that encompass the desired p-value. PRZM/EXAMS output is based on the Weibull plotting positions with a straight line interpolation between just the two data values that encompass the desired p-value of 0.100.

Appendix C: Ecological Effects Data

Overview

The toxicity testing required does not test all species of birds, fish, mammals, invertebrates, and plants. Only two surrogate species for birds (bobwhite quail and mallard) are used to represent all bird species (over 1000 in the US, including subspecies), three species of freshwater fish (rainbow trout, bluegill sunfish and fathead minnow) are used to represent all freshwater fish species (over 900 in the US), and one estuarine/marine fish species (sheepshead minnow) is used to represent all estuarine/marine fish (over 300 in the US). The surrogate species for terrestrial invertebrates is the honey bee, for freshwater invertebrates the surrogate species is usually the waterflea (*Daphnia magna*) and for estuarine/marine invertebrates the surrogate species are mysid shrimp and eastern oyster. These four species are used to represent all invertebrate species (over 10,000 in the US). For plants, there are ten surrogate species used for all terrestrial plants and five surrogate species used for all aquatic plants. There are over 20,000 plant species in the US which includes flowering plants, conifers, ferns, mosses, liverworts, hornworts and lichens with over 27,000 species of algae worldwide.

The surrogate species testing scheme used in this assessment assumes that a chemical's mechanism of action and toxicity found for avian species is similar to that in all reptiles (over 300 species in the US). The same assumption applies to amphibians (over 200 species in the US) and fish; the tadpole stage of amphibians is assumed to have the same sensitivity as a fish. Therefore, the results from toxicity tests on surrogate species are considered applicable to other member species within their class and are extrapolated to reptiles and amphibians. The US species numbers noted in this section were taken from the Natureserve website (www.natureserve.org NatureServe: An online encyclopedia of life [web application].2000) and the worldwide species number from Ecological Planning and Toxicology, Inc.1996.

In the following sections, the shaded values in the tables are the ones used in the current risk assessment.

a. Toxicity to Terrestrial Animals

i. Birds, Acute and Subacute

An acute oral toxicity study using the technical grade of the active ingredient (TGAI) is required to establish the toxicity of chloropicrin to birds. The avian oral LD_{50} is an acute, single-dose laboratory study designed to estimate the quantity of toxicant required to cause 50% mortality in a test population of birds. The preferred test species is either the mallard, a waterfowl, or bobwhite quail, an upland gamebird. The TGAI is administered by oral intubation to adult birds, and the results are expressed as LD_{50} milligrams (mg) active ingredient (a.i.) per kilogram (kg) of body weight. Toxicity category descriptions are the following:

If the LD_{50} is *less than 10 mg a.i./kg*, then the test substance is *very highly toxic*.

If the LD_{50} is *10-to-50 mg a.i./kg*, then the test substance is *highly toxic*.
If the LD_{50} is *51-to-500 mg a.i./kg*, then the test substance is *moderately toxic.*
If the LD_{50} is *501-to-2,000 mg a.i./kg*, then the test substance is *slightly toxic.*
If the LD_{50} is *greater than 2,000 mg a.i./kg*, then the test substance is *practically nontoxic.*

Acute oral testing on chloropicrin is needed for risk assessment.

Two dietary studies using the TGAI are usually required to establish the toxicity of pesticides to birds. These avian dietary LC_{50} tests, using the mallard and bobwhite quail, are acute, eight-day dietary laboratory studies designed to estimate the quantities of toxicant in the feed required to cause 50% mortality in the two respective test populations of birds. The TGAI is administered by mixture to juvenile birds' diets for five days followed by three days of "clean" diet, and the results are expressed as LC_{50} parts per million (ppm) active ingredient (a.i.) in the diet. Toxicity category descriptions are the following:

If the LC_{50} is *less than 50 ppm a.i.*, then the test substance is *very highly toxic*.
If the LC_{50} is *50-to-500 ppm a.i.*, then the test substance is *highly toxic*.
If the LC_{50} is *501-to-1,000 ppm a.i.*, then the test substance is *moderately toxic.*
If the LC_{50} is *1001-to-5,000 ppm a.i.*, then the test substance is *slightly toxic.*
If the LC_{50} is *greater than 5,000 ppm a.i.*, then the test substance is *practically nontoxic.*

However, dietary exposure is not considered to be the primary or even a substantial route of avian exposure to chloropicrin, and thus avian dietary toxicity data are not currently needed for risk assessment. Inhalation is expected to be the primary route of exposure and thus acute inhalation toxicity data on chloropicrin are needed for risk assessment.

ii. Birds, Chronic

Chronic/sub-chronic inhalation testing with chloropicrin is needed to assess risk to birds in part because of the potential for repeated or continuous exposure resulting from multiple fields being treated on differing days within a given geographic area.

iii. Mammalian Toxicity Data (from HED)

Chloropicrin Toxicity Profile (from HED 1/31/05 review)		
Guideline No./Study Type	**MRID No. (year)/Classification/Exposure Conditions**	**Results**

Chloropicrin Toxicity Profile (from HED 1/31/05 review)		
Guideline No./Study Type	**MRID No. (year)/Classification/Exposure Conditions**	**Results**
870.1100 Acute Oral - Rat	05014376 (1976) Acceptable/Guideline.	**LD_{50} = 37.5 mg/kg** **Toxicity Category I**
870.1200 Acute Dermal - Rat	05014376 (1976) Acceptable/Guideline	**LD_{50} = 100 mg/kg** **Toxicity Category I**
870.1300 Acute Inhalation - Mouse	45117901 (1999) Acceptable/Non-Guideline Head only study, 4 Albino Swiss-Webster male mice/grp exposed to 0.99, 3.20, 4.20, 7.25, 10.00, 14.50 ppm (analytical concen.)or 0.00664, 0.0215, 0.0282, 0.0486, 0.0671, 0.0973 mg/L (calculated analytical concen.)of gaseous CP for 30 mins.	No deaths seen at any dose level. Clinical obs. normal before and after exposure. Body wt. gains may been decreased at HDT only (8% of initial body wt. in control and 2% at the HDT). -The exposure level at 50% RD (RD50) was 2.34 ppm with 95% CI of 1.84 to 2.98 ppm or RD50 of 0.016 mg/L and 95% CI of 0.012 mg/L to 0.020 mg/L. -0% depression in the respiration rate was plotted by the % depression in the respiration rate reported in the study versus log exposure level and extrapolating the graph to 0% depression. The RD0 respiratory depression occurs around 0.0017 to 0.0019 mg/L.
870.1300 Acute Inhalation - Rat	45117902 (1999) Acceptable/Non-Guideline Whole body inhalation study, 5 Sprague Dawley rats/sex/grp were exposed to 0, 10.6, 18.0, or 28.5 ppm (analytical) or 0, 0.071, 0.121, 0.158 mg/L (calculated) of aerosolized CP for 4-hrs and held for 2 days after exposure. Particle sizes had a MMAD from 4.85 µm to 6.1µm with a GDS of 1.4 to 1.6.	LC50 [typo corrected] was 17 ppm (M) and 19 ppm (F). Death only occurred at 2 top dose levels up to 2 days post-exposure. Clinical signs: obs noted at all dose levels, labored breathing, gasping, decreased activity, nasal discharge, salivation, moist rales. Top 2 levels produced gasping for last 2 hrs of exposure. Gross pathology: Liver, adrenal wts, and histological findings increased at HDT. Histological findings of respiratory tract were seen at all dose levels and damage to the lungs, such as congestion, bronchiole mucosal edema, necrosis, and cellular infiltrates. -No NOAEL demonstrated. LOAEL = 10.6 ppm or 0.071 mg/L (LDT).
870.2400C Primary Eye Irritation - Rabbit	N/A	reserved

Chloropicrin Toxicity Profile (from HED 1/31/05 review)		
Guideline No./Study Type	**MRID No. (year)/Classification/Exposure Conditions**	**Results**
870.2500 Primary Skin Irritation - Rabbit	05014376 (1976) Acceptable/Guideline	Corrosive **Toxicity Category I**
870.2600 Dermal Sensitization	N/A	Reserved
870.3100 Subchronic Feeding - Rat		Not required by the Agency
870.3100 Subchronic Feeding - Mice		Not required by the Agency
870.3100 Subchronic Feeding - Mice		Not required by the Agency
870.3150 Subchronic Feeding - Dog		Not required by the Agency
870.3200 21-Day Dermal - Rat		Reserved
870.3465 13-Week Inhalation - Mouse	43063201 (1993) Acceptable/Guideline 0, 0.3, 1.0, or3.0 ppm in a whole-body chamber, 6 h/day, 5 days/week for 13 weeks	NOAEL = 0.3 ppm (0.002 mg/L/day) LOAEL = 1.0 ppm (0.007 mg/L/day) based on decreased body weight and food consumption, increased absolute and relative lung weights in both sexes, and histopathological lesions of the nasal cavity and lungs of females.
870.3465 13-Week Inhalation - Rat	43063201 (1993) Acceptable/Guideline 0, 0.3, 1.0, or3.0 ppm in a whole-body chamber, 6 h/day, 5 days/week for 13 weeks	NOAEL = 0.3 ppm (0.002 mg/L/day) LOAEL = 1.0 ppm (0.007 mg/L/day), based on increased lung weights of both sexes, and histopathological changes in the nose of females and lungs of males and females.
870.3700 Inhalation Developmental Toxicity - Rat	42740602 (1993) Acceptable/Guideline 0, 0.4, 1.2, or 3.5 ppm in a whole-body inhalation chamber, 6 h/day on GDs 6-15.	Maternal NOAEL = 0.4 ppm (0.003 mg/L/day) Maternal LOAEL = 1.2 ppm (0.008 mg/L/day) based on mortality, decreased body weight and food consumption, and signs consistent with CP toxicity. Developmental NOAEL > 3.5 ppm (0.024 mg/L) Developmental LOAEL= 3.5 ppm (0.024 mg/L), based on decreased pup body weights.

Chloropicrin Toxicity Profile (from HED 1/31/05 review)		
Guideline No./Study Type	**MRID No. (year)/Classification/Exposure Conditions**	**Results**
870.3700 Inhalation Developmental Toxicity - Rabbit	42740601 (1993) Acceptable/Guideline 0, 0.4, 1.2, or 2.0 ppm in a whole-body inhalation chamber, 6 h/day, on GDs 7-29.	Maternal NOAEL is 0.4 ppm (0.003 mg/L) Maternal LOAEL is 1.2 ppm (0.008 mg/L), based on mortality, body weight loss, and decreased food consumption. Developmental NOAEL= 0.4 ppm (0.003 mg/L) Developmental LOAEL= 1.2 ppm (0.008 mg/L), based on abortions and decreased fetal weights.
870.3800 Inhalation 2-Generation Reproductive Toxicity - (Main study) Rat	43391901 (1994) Acceptable/guideline 0, 0.5, 1.0, or 1.5 ppm in whole body inhalation chamber **Note: Offspring not directly exposed until PND 28**	Parental systemic NOAEL > 1.5 ppm (0.0101 mg/L) Parental systemic LOAEL not identified Offspring NOAEL > 1.5 ppm (0.0101 mg/L) Offspring LOAEL not identified Reproductive NOAEL > 1.5 ppm (0.0101 mg/L) Reproductive LOAEL not identified
870.3800 Range-finding, Inhalation 2-Generation Reproductive Toxicity - Rat	46427801 (conducted 1992, study report 1996) 0, 0.4, 1.0, or 2.0 ppm whole body for 6hrs/day, 7 days/week during premating (14 days) and gestation day 0-20.	No treatment-related mortality, clinical signs, or necropsy findings in any parental males or females, and no treatment-related effects on reproductive parameters. Mean body weight and weight gain decreased in high-dose group (1-3% M& 5-6% F) beginning at week 1. Maternal body weight was decreased 5-8% and decreased 17% during gestation. Food consumption decreased 8-14% in males and 14% in females during premating and 7% during gestation. Litter size decreased 33% and uterine implantation sites decreased 30% in the high-dose group.

Chloropicrin Toxicity Profile (from HED 1/31/05 review)		
Guideline No./Study Type	**MRID No. (year)/Classification/Exposure Conditions**	**Results**
870.4100 Chronic Feeding Toxicity-Rat	43744301 (1995) Acceptable/guideline Gavage at 0, 0.1, 1.0, or 10 mg/kg/day for 104 weeks.	Only clinical toxicity observed was salivation after dosing in high-dose male and female rats. Dose-related increase in incidence of subcutaneous masses of skin of females related to the increased incidence of mammary fibroadenomas. Hyper-keratosis and hyperplasia of the nonglandular stomach in both sexes. Females had dose-related increase in incidence of fibroadenoma of the mammary gland at high-dose. Increased rate of C-cell hyperplasia of the thyroid in high-dose females. NOAEL = 0.1 mg/kg/day [F] NOAEL = 1.0 mg/kg/day [M] LOAEL = 1.0 mg/kg/day [F], based on periportal hepatocyte vacuolation and thyroid C-cell hyperplasia and stomach lesions at the high-dose. LOAEL = 10 mg/kg/day [M], basedon on stomach lesions.
870.4100 Chronic Feeding Toxicity - Dog	43196301(1994) Acceptable/guideline 0, 0.1, 1.0, or 5.0 mg/kg/day for one year (capsule).	NOAEL [M] = 0.1 mg/kg/day NOAEL [F] = 1.0 mg/kg/day LOAEL [M] = 1.0 mg/kg/day, based on gastrointestinal irritation (vomiting and diarrhea), and blood chemistry alterations, LOAEL [F] = 5.0 mg/kg/day, based on gastrointestinal irritation (vomiting and diarrhea), microcytic hypochromatic anemia, and blood chemistry alterations.
870.4200 Carcinogenicity Inhalation - Mouse (78 weeks)	43632201 (1997) Acceptable/guideline 0, 0.1, 0.5, or 1.0 ppm for 78 weeks	NOAEL = 0.1 ppm (0.0007 mg/L) LOAEL = 0.5 ppm (0.0034 mg/L), based on systemic toxicity and irritation, based on decreased body weights and gains, increased lung weights, and histological changes in the nasal cavity, upper respiratory tract and lungs. No significant treatment-related increase in tumors.

Chloropicrin Toxicity Profile (from HED 1/31/05 review)		
Guideline No./Study Type	**MRID No. (year)/Classification/Exposure Conditions**	**Results**
870.4200 Carcinogenicity/gavage-Mouse/Rat [bioassay]	05014915 (1978) supplemental Rats: [M]: 0, 25 or 26 mg/kg/day [F]: 0, 20, or 22 mg/kg/day Mice [M]: 0, 66 mg/kg/day [F]: 0, 33 mg/kg/day	High-incidence of early death in CP dose rats. No neoplasm observed at higher incidences in dosed rats from controls. Rapid decrease in survival after first year in both sexes of mice. Proliferative lesions of squamous epithelium of the forestomach of mice included two carcinomas and a papilloma. Statistical analysis did not demonstrate related to CP. Bioassay of CP did not permit evaluation of carcinogenicity due to short survival time of mice and rats.
870.4300 Chronic Inhalation Toxicity/Carcinogenicity-Rat. (2 year)	43755301 (1995) Acceptable/guideline 0, 0.15, 0.5, or 1.0 ppm in a whole body inhalation chamber for 6 hrs/day, 5days/week for up to 108 weeks.	NOAEL =0.1 ppm (0.0007 mg/L) LOAEL = 0.5 ppm (0.0034 mg/L), based on increased mortality rate and decreased mean survival time in males, and transiently decreased body weight gains in both sexes. Port of entry NOAEL = 0.5 ppm Port of entry LOAEL = 1.0 ppm (males), based on severe rhinitis of the anterior nasal cavity.
870.5100 Bacterial Reverse Mutation Test (Ames Assay)	41960801 (1990) Acceptable/guideline	S9-activated CP is Mutagenic in *Salmonella typhimurium* strains TA98,and TA100.
870.5300 *Mutagenic*-Lymphoma Mutation-Mouse	41960803 (1990) Acceptable/guideline	CP ranging from 0.038 to 0.75 nL/mL-S9 and 0.89 to 16 nL/mL +S9 did not induce a mutagenic response in two independently performed mouse lymphoma forward mutation assays.
870.5375 *In Vitro* Chromosomal Aberration in Chinese Hamster Ovary	41960802 (1990) Acceptable/guideline	Nonactivated doses of CP from 0.75 to 1 nL/mL induced a reproducible and significant clastogenic response in Chinese hamster ovary (CHO) cells harvested 12 hours post-treatment. Nonactivated CP was clastogenic over a narrow range of cytotoxic concentrations. CP in the absence of S9 activation is a clastogen in this mammalian test system.
870.5395 Unscheduled DNA Synthesis-Rat	41960804 (1990) Acceptable/guideline	CP was not genotoxic in primary rat hepatocytes over a concentration range (0.3 to 6 nL/mL) that included moderately cytotoxic levels. CP showed no evidence of UDS.

Chloropicrin Toxicity Profile (from HED 1/31/05 review)		
Guideline No./Study Type	**MRID No. (year)/Classification/Exposure Conditions**	**Results**
870.6200 Inhalation Acute Neurotoxicity - Rats		Not required by the Agency
870.6200 Feeding Subchronic Neurotoxicity - Rats		Not required by the Agency
870.7485 Metabolism - Rat		Not available.
870.7600 Dermal Penetration - Rat		Not required by the Agency

b. Toxicity to Freshwater Aquatic Animals

i. Freshwater Fish, Acute

Two freshwater fish toxicity studies using the TGAI are required to establish the toxicity of chloropicrin to fish. The preferred test species are rainbow trout (a coldwater fish) and bluegill sunfish (a warmwater fish). Results of these tests are tabulated below. The toxicity category descriptions for freshwater and estuarine/marine fish and aquatic invertebrates, are defined below in parts per million (ppm).

If the LC_{50} is *less than 0.1 ppm a.i.*, then the test substance is *very highly toxic*.
If the LC_{50} is *0.1-to-1.0 ppm a.i.*, then the test substance is *highly toxic*.
If the LC_{50} is *greater than 1 and up through 10 ppm a.i.*, then the test substance is *moderately toxic.*
If the LC_{50} is *greater than 10 and up through 100 ppm a.i.*, then the test substance is *slightly toxic.*
If the LC_{50} is *greater than 100 ppm a.i.*, then the test substance is *practically nontoxic.*

Table 3: Freshwater Fish Acute Toxicity - Chloropicrin Technical

Species/ Flow-through or Static	% ai	LC_{50} (ppb)	Toxicity Category	MRID/Accession (ACC) No. Author/Year	Study Classification
Bluegill Sunfish *(Lepomis macrochirus)*/Static	99.0	<105	at least highly toxic	FTLR 439/McCann/1972	Suppl.
Rainbow Trout (Oncorhynchus sp.)/Static	99.0	< 16.98	Very highly toxic	FTLR 425/McCann/1971	Suppl.

The requirement for two freshwater fish acute toxicity studies has not been satisfied. Flow-through studies with measured concentrations are needed to reduce uncertainty in the risk assessment.

ii. Freshwater Fish, Chronic

A freshwater fish early life-stage test is required for chloropicrin since it is expected to be transported to water from the intended use site, and one or more of the following conditions are met: (1) the pesticide is intended for use such that its presence in water is likely to be continuous or recurrent, (2) any aquatic acute LC_{50} or EC_{50} is less than 1 ppm, and/or (3) the EEC in water is equal to or greater than 0.01 of any acute LC_{50} or EC_{50} value. The preferred test species is rainbow trout.

The fish early life-stage is a laboratory test designed to estimate the quantity of toxicant required to adversely effect the reproduction of a test population of fish. The test should be performed using flow-through conditions. The test material is administered into water containing the test

species, providing exposure throughout a critical life-stage, and the results, generally, are expressed as a No Observed Adverse Effect Concentration (NOAEC) in parts per million or parts per billion of active ingredient. The No Observed Adverse Effect Concentration represents an exposure concentration, at or below which biologically significant effects will not occur to species of similar sensitivities.

(iii) Freshwater Invertebrates, Acute

A freshwater aquatic invertebrate toxicity test using the TGAI is required to establish the toxicity of chloropicrin to aquatic invertebrates. The preferred test organism is *Daphnia magna*, but early instar amphipods, stoneflies, mayflies, or midges may also be used. Results of this test are tabulated below.

Table 5: Freshwater Invertebrate Acute Toxicity - Chloropicrin

Species/ Flow-through or Static	% ai	LC_{50}/EC_{50} (ppb)	Toxicity Category	MRID/Accession (ACC) No. Author/Year	Study Classification
Daphnid *(Daphnia pulex)*/static	$\geq$ 96.5	< 71	very highly toxic	130704/Cody and Shema/1983	Supplemental

[1] Core (study satisfies guideline). Supplemental (study is scientifically sound, but does not satisfy guideline).

The requirement for an acute freshwater invertebrate acute toxicity study has not been satisfied. A flow-through study with measured concentrations is needed to reduce uncertainty in the risk assessment.

iv. Freshwater Invertebrate, Chronic

A freshwater aquatic invertebrate life-cycle test is required for chloropicrin because this degradate is expected to be transported to water from the intended use site, and one or more of the following conditions are met: (1) the pesticide is intended for use such that its presence in water is likely to be continuous or recurrent, (2) any aquatic acute LC_{50} or EC_{50} is less than 1ppm, and/or (3) the EEC in water is equal to or greater than 0.01 of any acute LC_{50} or EC_{50} value. A flow-through study with measured concentrations is needed for risk assessment.

c. Toxicity to Estuarine and Marine Animals

i. Estuarine and Marine Fish, Acute

Acute toxicity testing with estuarine/marine fish is required for chloropicrin since the active ingredient and or degradates are expected to reach the marine/estuarine environment due to its expected use in coastal counties. The preferred test species is the sheepshead minnow.

ii. Estuarine and Marine Fish, Chronic

An estuarine/marine fish early life-stage toxicity test using chloropicrin is reserved, pending submission and review of freshwater fish chronic testing.

iii. Estuarine and Marine Invertebrates, Acute

Acute toxicity testing with estuarine/marine invertebrates is required for chloropicrin because it is expected to reach the marine/estuarine environment due to its expected use in coastal counties. The preferred test species are mysid shrimp and eastern oyster.

iv. Estuarine and Marine Invertebrate, Chronic

An estuarine/marine invertebrate life-cycle toxicity test (Guideline 72-4b) using chloropicrin is reserved, pending submission and review of freshwater invertebrate chronic testing.

d. Toxicity to Plants

i. Terrestrial Plants

Terrestrial plant Tier I seedling emergence and vegetative vigor testing of a Typical End-Use product (TEP) is currently recommended for all pesticides having outdoor uses (EFED Policy, Keehner. July 1999). For seedling emergence and vegetative vigor testing, the following plant species and groups should be tested: (1) six species of at least four dicotyledonous families, one species of which is soybean (*Glycine max*) and the second is a root crop, and (2) four species of at least two monocotyledonous families, one of which is corn (*Zea mays*). Tier I tests measure the response of plants, relative to a control, at a test level that is equal to the highest use rate expressed as pounds active ingredeint per acre (lbs ai/A). Tier II studies are required if the Tier I studies indicate any of the test species, when exposed to the test material, displayed a ≥25% inhibition or over-enhancement of various growth parameters as compared to the control. This guideline has not been satisfied.

ii. Aquatic Plants

Aquatic plant testing is recommended for all pesticides having outdoor uses (EFED Policy, Keehner. July 1999). The tests are performed on species from a cross-section of the aquatic plant population. The preferred test species are duckweed (*Lemna gibba*), marine diatom (*Skeletonema costatum*), blue-green algae (*Anabaena flos-aquae*), freshwater green alga (*Selenastrum capricornutum*), and a freshwater diatom. Tier I aquatic plant testing is a maximum dose test

designed to quickly evaluate the toxic effects to the test species in terms of growth and reproduction and to determine the need for additional aquatic plant testing. Tier II aquatic plant testing is a multiple dose test of the plants species that showed a phytotoxic effect to the pesticide being tested at the Tier I level. Tier II testing is designed to determine the detrimental effect levels of the chemical on the aquatic plants which showed a greater than 50% detrimental effect in Tier I testing.

e. Toxicity to Non-target Insects

An acute contact study with the honey bee (141-1) is required, since the proposed uses are outdoors.

Appendix D. The Risk Quotient Method and Levels of Concern

Risk characterization integrates the results of the exposure and ecotoxicity data to evaluate the likelihood of adverse ecological effects. The means of this integration is called the quotient method. Risk quotients (RQs) are calculated by dividing exposure estimates by acute and chronic ecotoxicity values.

RQ = EXPOSURE/TOXICITY

RQs are then compared to OPP's levels of concern (LOCs). These LOCs are used by OPP to analyze potential risk to nontarget organisms and the need to consider regulatory action. The criteria indicate that a pesticide used as directed has the potential to cause adverse effects on nontarget organisms. LOCs currently address the following risk presumption categories: (1) acute risks - regulatory action may be warranted in addition to restricted use classification, (2) acute restricted use - the potential for acute risk is high, but may be mitigated through restricted use classification, (3) acute endangered species - endangered species may be adversely affected, and (4) chronic risk - the potential for chronic risk is high regulatory action may be warranted. Currently, EFED does not perform assessments for chronic risk to plants, acute or chronic risks to insects, or chronic risk from granular/bait formulations to birds or mammals.

The ecotoxicity test values (measurement endpoints) used in the acute and chronic risk quotients are derived from required studies. Examples of ecotoxicity values derived from short-term laboratory studies that assess acute effects are: (1) LC_{50} (fish and birds), (2) LD_{50} (birds and mammals), (3) EC_{50} (aquatic plants and aquatic invertebrates) and (4) EC_{25} (terrestrial plants). Examples of toxicity test effect levels derived from the results of long-term laboratory studies that assess chronic effects are: (1) LOAEL or LOAEC (birds, fish, and aquatic invertebrates) and (2) NOAEL or NOAEC (birds, fish and aquatic invertebrates). For birds, mammals, fish and aquatic invertebrates the NOAEL or NOAEC generally is used as the ecotoxicity test value in assessing chronic effects, although other values may be used when justified. Risk presumptions and the corresponding RQs and LOCs, are tabulated below.

Table 1. Risk presumptions for terrestrial animals based on risk quotients (RQ) and levels of concern (LOC).

Risk Presumption	RQ	LOC
	Birds	
Acute Risk	**EEC[1]/LC_{50} or LD_{50}/ft^2 or LD_{50}/day[3]**	**0.5**
Acute Restricted Use	**EEC/LC_{50} or LD_{50}/ft^2 or LD_{50}/day (or LD_{50} < 50 mg/kg)**	**0.2**
Acute Endangered Species	**EEC/LC_{50} or LD_{50}/ft^2 or LD_{50}/day**	**0.1**
Chronic Risk	**EEC/NOAEC**	**1**
	Wild Mammals	
Acute Risk	**EEC/LC_{50} or LD_{50}/ft^2 or LD_{50}/day**	**0.5**
Acute Restricted Use	**EEC/LC_{50} or LD_{50}/ft^2 or LD_{50}/day (or LD_{50} < 50 mg/kg)**	**0.2**
Acute Endangered Species	**EEC/LC_{50} or LD_{50}/ft^2 or LD_{50}/day**	**0.1**
Chronic Risk	**EEC/NOAEC**	**1**

[1] abbreviation for Estimated Environmental Concentration (ppm) on avian/mammalian food items
[2] mg/ft^2
[3] mg of toxicant consumed/day
LD_{50} * wt. of bird
LD_{50} * wt. of bird

Table 2. Risk presumptions for aquatic animals based on risk quotients (RQ) and levels of concern (LOC).

Risk Presumption	RQ	LOC
Acute Risk	**EEC[1]/LC_{50} or EC_{50}**	**0.5**
Acute Restricted Use	**EEC/LC_{50} or EC_{50}**	**0.1**
Acute Endangered Species	**EEC/LC_{50} or EC_{50}**	**0.05**
Chronic Risk	**EEC/NOAEC**	**1**

[1] EEC = (ppm or ppb) in water

Table 3. Risk presumptions for plants based on risk quotients (RQ) and levels of concern (LOC).

Risk Presumption	RQ	LOC
	Terrestrial and Semi-Aquatic Plants	
Acute Risk	EEC[1]/EC_{25}	1
Acute Endangered Species	EEC/EC_{05} or NOAEC	1
	Aquatic Plants	
Acute Risk	EEC[2]/EC_{50}	1
Acute Endangered Species	EEC/EC_{05} or NOAEC	1

[1] EEC = lbs ai/A
[2] EEC = (ppb/ppm) in water

Appendix E. Data Requirement Tables

Table A1(A). Ecological Effects Data Requirements for: Chloropicrin

Guideline #	Data Requirement	Are Additional Data Needed for Risk Assessment?	MRID #'s	Study Classification
71-1(a)	Avian Acute Oral	Y	----------	----------
------	Avian Acute Inhalation	Y	----------	----------
71-2(a)	Avian Dietary–quail	N	----------	----------
71-2(b)	Avian Dietary–mallard	N	----------	----------
---------	Avian Subchronic/Chronic Inhalation	Y	----------	----------
72-1(a)	Fish Acute Toxicity–bluegill	Y	FTLR 439	S
72-1(b)	Fish Acute Toxicity–rainbow trout	Y	FTLR 425	S
72-2(a)	Aquatic Invertebrate Acute Toxicity–freshwater	Y	130704	S
72-3(a)	Marine/Estuarine Acute Toxicity–Fish	Y	----------	----------
72-3(b)	Marine/Estuarine Acute Toxicity–Mollusk (shell deposition)	Y	----------	----------
72-3(c)	Marine/Estuarine Acute Toxicity–Shrimp	Y	----------	----------
72-4(a)	Fish Early Life Stage–freshwater	Y	----------	----------
72-4(a)	Fish Early Life Stage– marine/estuarine	Reserved	----------	----------
72-4(b)	Aquatic Invertebrate Life Cycle–freshwater	Y	----------	----------
123-1(a)	Seedling Germination/Seedling Emergence–Tier II	Y	----------	----------
123-1(b)	Vegetative Vigor–Tier II	Y	----------	----------
123-2	Aquatic Plant Growth – Tier II	Y		----------
141-1	Honeybee Acute Contact	Y	----------	----------

A=Acceptable; S=Supplemental; U=Unnaceptable; W=Waived; N/A=Not Applicable; NA=Not Available; Inv.=Invalid; R=Potentially Repairable

Table 1A (B). Environmental Fate Data Requirements for: Chloropicrin

Guideline #	Data Requirement	Is Data Requirement Satisfied?	MRID #'s	Study Classification
161-1	Hydrolysis	Y	43022401	A
161-2	Photodegradation in Water	Y	42900201	S
161-3	Photodegradation on Soil	N/A	NA	W
161-4	Photodegradation in Air	Y	05007865	A
162-1	Aerobic Soil Metabolism	Y	43613901	S
162-2	Anaerobic Soil Metabolism	N/A	----------	----------
162-3	Anaerobic Aquatic Metabolism	Y	43759301	S
162-4	Aerobic Aquatic Metabolism	N/A	----------	----------
163-1	Mobility-Column Leaching	Y	44191301	S
163-2	Laboratory Volatility	Y	43798601	A
163-3	Field Volatility	Reserved	----------	----------
164-1	Terrestrial Field Dissipation	N	43085101	S
165-4	Accumulation in Fish/ Bioconcentration	N/A	NA	W

A=Acceptable; S=Supplemental; U=Unnaceptable; W=Waived; N/A=Not Applicable; NA=Not Available